The Catalytic Chain Transfer Emulsion Polymerisation of Acrylic Monomers

by

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Declaration

All experimental work contained in this thesis is original research that was carried out by the author in the Department of Chemistry, University of Warwick, between October 1996 and October 1999. No material contained herein has been submitted for any other degree to this, or any other, institution.

Results from other authors are referenced in the usual manner throughout the text.

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David Morsley

Abstract

This thesis has explored the synthesis of macromonomers by Catalytic Chain Transfer (CCT) emulsion polymerisation.

It has been shown that the effective synthesis of methacrylate macromonomers using catalyst concentrations below a threshold level is not possible since the viscosity in the particles becomes too high to allow efficient movement of the CCT agent between latex particles. It has been demonstrated that an addition of a shot of monomer at the start of the reaction is necessary to allow effective CCT to occur.

The addition of the water soluble methacrylate monomer HEMA to a methyl methacrylate CCT emulsion polymerisation was shown to have little effect on the transfer reaction. Macromonomers consisting of a statistical mixture of MMA and HEMA can therefore be easily prepared by CCT emulsion polymerisation.

The results of CCT emulsion polymerisations where the synthesis of butyl acrylate/ methyl methacrylate macromonomers were attempted were also outlined and effective macromonomer synthesis was observed for low amounts of acrylate. For higher amounts of acrylate it was observed that effective macromonomer synthesis was only observed up to moderate conversions.

The synthesis of methacrylic acid containing macromonomers using CCT emulsion polymerisation was studied and it was shown that controlled macromonomer synthesis could only be carried out at low methacrylic acid concentrations.

Results described show that the effectiveness of the CCT emulsion polymerisation process is very dependant on the solublity of the catalyst. The more the CCT agent is soluble in the monomer and hence particle phase the greater the observed transfer constant. If the catalyst is too soluble in the monomer the observed transfer constant is greatly reduced due to the inability of the catalyst to transport from the monomer droplets to the particles effeciently.

Abbreviations

BA	Butyl acrylate
BMA	Butyl methacrylate
CCT	Catalytic Chain Transfer
COBF	Cobaloxime Boron Fluoride
COPhBF	Tetra-phenyl-cobaloxime Boron Fluoride
Cs	Chain transfer constant
Cs^E	Effective chain transfer constant in emulsion
DP	Degree of polymerisation
DSC	Differential scanning calorimetry
f_x	Fraction of monomer x in the feed
F_x	Fraction of monomer x in the polymer
HEMA	Hydroxyethyl methacrylate
k_p	Rate of propagation
k_t	Rate of termination
$k_{t,c}$	Rate of termination by combination
$k_{t,d}$	Rate of termination by disproportionation
k_{tr}	Rate of transfer
MMA	Methyl methacrylate
M_n	Number average molecular weight
M_w	Weight Average molecular weight
NMR	Nuclear magnetic resonance
PDi	Polydispersity index
PMMA	Poly (methyl methacrylate)

PPM	Parts per million
SEC	Size exclusion chromatography
T_g	Glass transition temperature
$T_{g,\infty}$	Limiting glass transition temperature at infinite molecular weight
TGA	Thermal gravimetric analysis

Chapter 1

Literature Review

1.1 Free radical polymerisation

Free radical polymerisation is the most commonly used of the polymerisation techniques with vast quantities of bulk polymer products being manufactured world wide by this polymerisation method. Free radical polymerisation can be used to synthesise a wide range of different polymer products and the tolerance of the reaction to trace impurities and oxygen in the system make the reaction very commercially successful.

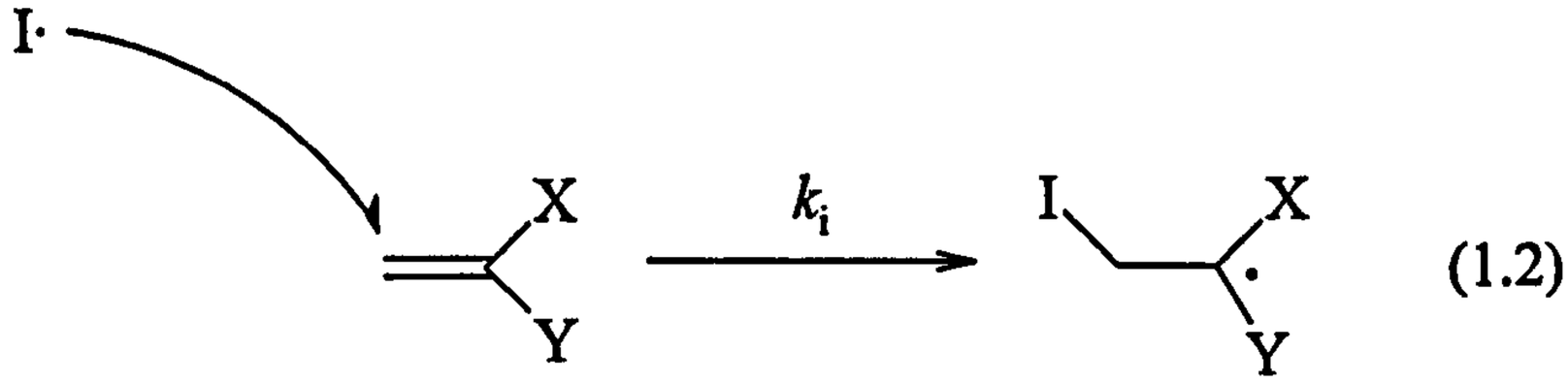
The mechanism of free radical polymerisation can be conveniently divided into four main processes: Initiation, Propagation, Chain Transfer and Termination[1-4]. These steps will be described in turn.

1.1.1 Initiation

The first stage of a free radical polymerisation is the formation of the primary radicals. This is usually achieved either by the thermal decomposition of an initiator molecule (equation 1.1), or by the action of a redox reaction or photochemical reaction.

$$I_2 \xrightarrow{k_d} 2I\cdot \qquad (1.1)$$

Once the reactive radical had been formed it can attack the double bond of an unsaturated compound. Generally head - to - tail addition is favoured since the electron donating groups, X and Y, on the monomer stabilise the radical , as shown in equation 1.2.



(1.2)

The initiation reactions are given the rate coefficients k_d and k_i for the rate of decomposition of the initiator and rate of reaction of the initiator radical with a monomer molecule respectively.

1.1.2 Propagation

Propagation is the main chain growth part of the free radical polymerisation reaction. In this process monomer units are added sequentially to the polymer chain thus increasing the chain length. A monomeric radical (formed in equation 1.2) attacks a further monomer molecule yielding a dimeric radical (equation 1.3). The dimeric radical can then attack a further monomer unit and so on extending the polymer chain. The many reactions that encompass the propagation steps are summarised in figures 1.3 and 1.4.

$$M_n^{\bullet} + M \xrightarrow{k_p} M_{n+1}^{\bullet} \qquad (1.3)$$

$$M_{n+1}^{\bullet} + M \xrightarrow{k_p} M_{n+2}^{\bullet} \qquad (1.4)$$

M in equations 1.3 and 1.4 is a monomer molecule and $M_n^{\bullet}$ is the propagating polymer radical with n number of monomer units. The rate coefficient k_p describes the rate of propagation. Assigning k_p to the reactions in equation 1.3 and 1.4 assumes that all chain lengths of polymer radicals react with a monomeric unit at an identical rate; i.e. the rate of propagation is chain length independent. There is evidence to suggest however that short-chained radicals propagate very much faster than their long chained counterparts[3].

The rate of propagation should not be confused with the rate of polymerisation (the rate at which the monomer is consumed) as this will also depend upon the rate of initiation and termination; the equation for the rate of polymerisation will be derived later in section 1.1.5.

1.1.3 Chain Transfer

Chain transfer is a chain stopping event which usually involves the abstraction of a hydrogen or other atom from monomer, solvent, initiator or other species in the polymerisation medium (see equation 1.5).

$$M_n^{\bullet} + XA \xrightarrow{k_{tr}} M_nX + A^{\bullet} \qquad (1.5)$$

$$A^{\bullet} + M \xrightarrow{k_i^{tr}} AM^{\bullet} \qquad (1.6)$$

Although chain transfer does shorten the chains in a polymerisation, i.e. it reduces the molecular weight; it should not affect the rate of polymerisation since the chain transfer reaction does not change the concentration of radicals in the system.

A compound may be deliberately added to a polymerisation medium to act as a chain transfer agent and hence lower the chain length. Typically such compounds have an easily abstractable hydrogen or halogen atom, which may be taken by the propagating radical chain; examples of chain transfer compounds commonly used are mercaptans and amines. The activity of a chain transfer agent can be assessed using the Mayo equation (equation 1.7).

$$\frac{1}{DP} = \frac{1}{DP_0} + C_s\left(\frac{[S]}{[M]}\right) \quad (1.7)$$

DP is the degree of polymerisation or number of monomer repeat units, DP_0 is the degree of polymerisation in the absence of chain transfer agent. $[S]$ and $[M]$ are the concentrations of transfer agent and monomer respectively and C_s is the chain transfer constant. A transfer constant of around 10 is usual for mercaptans in a methyl methacrylate polymerisation [4].

1.1.4 Termination

There are two main ways in which a growing polymer radical can terminate to give a 'dead' polymer chain, (1) combination or (2) disproportionation. Combination, as the name suggests, involves the direct joining of two propagating chains to give one dead polymer, as illustrated in equation 1.8.

$$M_i^{\bullet} + M_j^{\bullet} \xrightarrow{k_{t,c}} P_{i+j} \quad (1.8)$$

Alternatively two polymer radicals may terminate by disproportionation where a hydrogen atom is transferred between chains, one chain being left with an

unsaturated endgroup and the other is left with a saturated one (this is represented schematically in equation 1.9).

$$M_i^{\bullet} + M_j^{\bullet} \xrightarrow{k_{t,d}} P_i + P_j \qquad (1.9)$$

Generally in polymerisation systems there is a mixture of termination types, with both combination and disproportionation being present. The extent of each termination type is monomer dependent, with methyl methacrylate observing a high amount of disproportionation due to there being three β - hydrogens available for transfer whereas styrene terminates entirely by combination. The exact amount of termination by disproportionation is dependent on the reaction temperature with the fraction for methyl methacrylate being 67% at 25 °C and 80% at 80 °C[4].

1.1.5 Overall Rate of Polymerisation

The overall rate of polymerisation R_p can be expressed as in equation 1.10.

$$R_p = k_p[M][M_n\cdot] \quad (1.10)$$

[M] represents the concentration of monomer present and [$M_n^{\cdot}$] is the concentration of all polymer chain radicals from n=1 (i.e. monomeric radical) upwards. [$M_n^{\cdot}$] is dependant on the rates of initiation (R_i in equation 1.11) and termination (R_t in equation 1.12) since these reactions will affect the concentration of radicals in the system.

$$R_i = 2k_d f[I_2] \qquad (1.11)$$

In the equation for rate of initiation (R_i), the symbol f signifies the efficiency of the initiator and represents how many polymer chains are actually started by the radicals that are formed (1.9). The initiator efficiency term is necessary due to the occurrence of chain transfer to initiator and other reactions that do not result in the initiation of polymer chains.

The expression for the rate of termination R_t does not discriminate between chains terminated by disproportionation and combination (equation 1.12).

$$R_t = 2k_t[M\cdot]^2 \qquad (1.12)$$

If a steady state assumption is made that the concentration of radicals is low and does not change through the course of the reaction, we can state that the rate of termination is equal to the rate of initiation i.e. $R_t = R_i$ and it is then possible to write equation 1.13 and rearrange to give 1.14.

$$2k_t[M\cdot]^2 = 2k_d f[I_2] \qquad (1.13)$$

$$[M\cdot] = \left(\frac{2k_d f[I_2]}{2k_t}\right)^{1/2} \qquad (1.14)$$

Equation 1.14 gives an expression for the concentration of radicals in the system and if this is inserted into equation 1.10 then the rate of polymerisation can be determined by equation 1.15.

$$R_p = k_p[M]\left(\frac{2k_d f[I_2]}{2k_t}\right)^{1/2} \qquad (1.15)$$

1.1.5.1 Measuring the Rate of Polymerisation

The simplest method for the determination of the rate of polymerisation is by measuring conversion as a function of time by gravimetry. A sample of the reaction solution is taken and weighed, the monomer is then removed by evaporation or precipitation and the sample re-weighed: The percentage conversion is then calculated, which represents the amount of monomer which has been converted to polymer. Other techniques available for measuring the percentage conversion include NMR spectroscopy and dilatometry. If a sample of the reaction mixture is taken, the ratio of remaining monomer to formed polymer may be calculated by analysing the integrals of specific peaks in the NMR spectrum. Dilatometry may be used for an on-line method of conversion analysis by measuring the change in volume of the reaction mixture as monomer is converted to polymer.

In some methods of polymerisation, a feed of monomer into the reaction vessel is required and so it is often useful to quote the *instantaneous conversion* of a polymerisation. The *instantaneous conversion* is the conversion of the polymerisation calculated at a particular moment in time representing the actual amount of monomer that has been added to the reactor and is available for polymerisation.

1.2 Molecular Weight

The molecular weight of a polymer has an effect on its physical properties and so the determination of the molecular weight is often important. The mechanism by which most polymers are made means that a sample of polymer will not consist of one discreet molecular weight but will be a mixture of many different chain lengths. It is often necessary to define not only an average molecular weight but also to describe the breadth of the distribution produced, i.e. does the polymer sample consist of a narrow range of molecular weights or a wide range? The molecular weight often quoted for polymer molecular weight is the *number average* molecular weight (M_n) which is defined as in equation 1.16.

$$\overline{M_n} = \frac{\sum N_i M_i}{\sum N_i} \qquad (1.16)\ \textit{Number average molecular weight}$$

$$\overline{M_w} = \frac{\sum N_i M_i^2}{\sum N_i M_i} \qquad (1.17)\ \textit{Weight average molecular weight}$$

N_i refers to the number of polymer chains with molecular weight M_i. It is also possible to define a weight average molecular weight (M_w), which is shown in equation 1.17, which is biased to higher molecular weight than M_n. The *polydispersity index* (PDI) of a polymer sample is defined as in equation 1.18 and represents the breadth of the polymer distribution.

$$PDI = \overline{M_w} / \overline{M_n} \qquad (1.18)\ \textit{Polydispersity index}$$

Currently the method of choice for the determination of the molecular weight of a polymer sample is size exclusion chromatography (also called gel permeation chromatography). If a solution of polymer is passed down a specially prepared column of crosslinked polystyrene the sample will be separated according to molecular weight. The polystyrene contains pores of differing sizes that will allow polymer molecules of different molecular weights (actually hydrodynamic volumes) to pass through the column at different speeds. Polymer chains of high molecular weight pass straight down the column without entering the pores and are eluted first and small molecules (which can enter the pores) take longer to pass through and are eluted last. When the column has separated the polymer molecules they are commonly detected by the change in refractive index of the solution. With a proper calibration with known standards it is possible to obtain M_n , M_w and polydispersity data from the SEC results.

Once the molecular weight has been determined, by whichever method is used, it is often useful to convert the value to the number of repeat units per chain or D_p. The simple relationship $M_n/M_0 = D_p$ can be used, where M_0 is the molecular weight of the repeat unit. If a co-polymer is used (see section 1.4) then M_0 will refer to the average repeat unit.

1.3 Polymer Structure

Unlike conventional small molecules polymers do not usually have a simple crystalline solid state structure[2,4]. In any given polymer sample there may be both ordered and unordered regions, which are the crystalline and amorphous regions of the polymer. The degree of crystallinity of a polymer varies depending on the chemical make up of the material. The thermal behaviour of a polymer sample (below decomposition temperatures) will depend on the two regions in the polymer. A melting temperature (T_m) describes the melting of the crystalline regions of the polymer sample and a glass transition temperature (T_g) describes the transition of the unordered part of the polymer going from an amorphous state to a glassy state. A characteristic increase in brittleness and rigidity of the sample occurs on the transition from a rubber to a glass. The glass transition temperature of polymer is often measured using the technique of differential scanning calorimetry (DSC). This technique is performed by heating the polymer at set rate and the heat flow required to keep the sample the same temperature as a reference sample is measured. Other techniques that are used for the measurement of glass transition temperature include dynamic mechanical behaviour and measuring the specific volume change using the technique of dilatometry.

1.4 Co-polymerisation

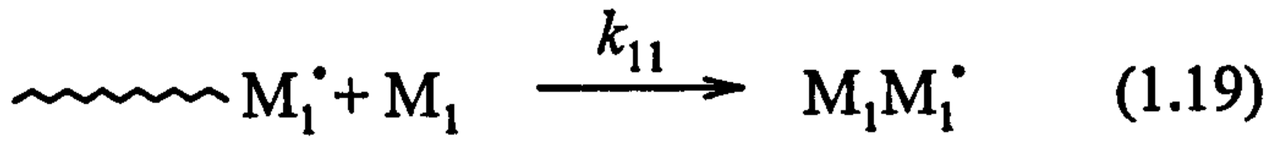
Most commercial synthetic polymers are not made up of only one monomer but are co-polymers i.e. polymers which have two or more monomers mixed

together, usually in a statistical fashion. In many cases the additional monomer may only represent a few percent of the total mass of the polymer but this may be enough to change the properties of the end product. Such properties that are often affected by co-polymerising multiple monomers are the melting point, glass transition, crystallinity and mechanical properties. It is also possible to mix different types of chemical functional groups into one polymer chain, which can lead to the synthesis of materials such as surfactants and polymer stabilisers.

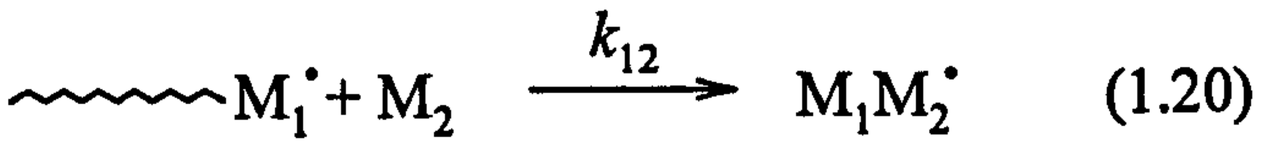
1.4 .1 Types of Co-polymers

1.4.1.1 Statistical Co-polymers

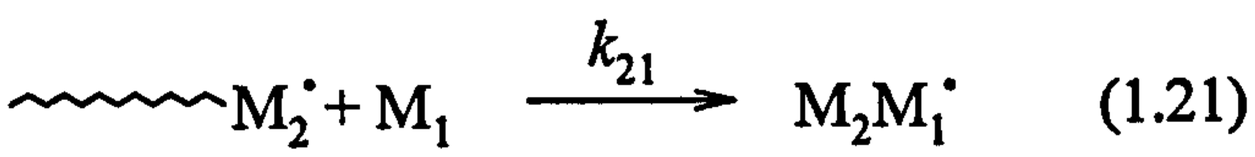
Statistical or *random* co-polymerisation occurs by mixing the relevant monomers together and polymerising them by the method described in section 1.1. Unfortunately the monomers will very rarely have equal reactivity with each other and thus one monomer will tend to be consumed faster in a polymerisation than the other. It is therefore often necessary to 'feed' one of the monomers into the polymerisation mixture in order to keep compositional heterogeneity. In the *terminal model* of co-polymerisation it is assumed that only the end unit on a propagating polymer radical chain affects the addition of the subsequent monomer. In a two monomer polymerisation the *terminal model* predicts four possible reactions[5], which are shown in equations 1.19 – 1.22.



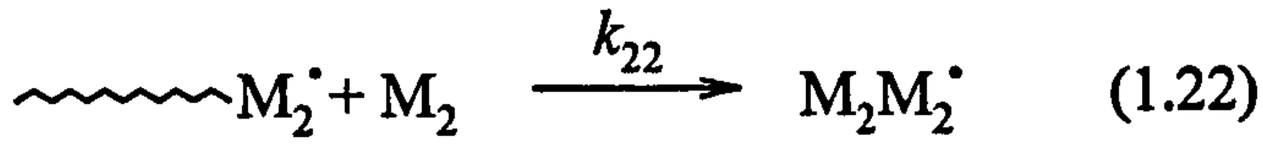
$$\sim\sim\sim\sim\sim M_1^{\bullet} + M_1 \xrightarrow{k_{11}} M_1M_1^{\bullet} \qquad (1.19)$$



$$\sim\sim\sim\sim\sim M_1^{\bullet} + M_2 \xrightarrow{k_{12}} M_1M_2^{\bullet} \qquad (1.20)$$



$$\sim\sim\sim\sim\sim M_2^{\bullet} + M_1 \xrightarrow{k_{21}} M_2M_1^{\bullet} \qquad (1.21)$$



$$\sim\sim\sim\sim\sim M_2^{\bullet} + M_2 \xrightarrow{k_{22}} M_2M_2^{\bullet} \qquad (1.22)$$

From the reactions described in 1.19-1.22 it is possible to assign reactivity ratios for the set of monomers M_1 and M_2 as defined in equations 1.23 and 1.24.

$$r_1 = \frac{k_{11}}{k_{12}} \qquad (1.23) \qquad r_2 = \frac{k_{22}}{k_{21}} \qquad (1.24)$$

The reactivity ratios shown above are useful in predicting the compositional drift of the polymer formed during a polymerisation reaction; for example, if two monomers are polymerised which have r_1 and r_2 of 4 and 0.1 respectively it would be possible to predict that monomer 1 (M_1) will be consumed very much faster in the polymerisation than monomer 2 (M_2). The consequence of this is that even if an equimolar mixture of the two monomers were polymerised, early in the polymerisation the polymer would be rich in M_1 and late on in the reaction (when all M_1 had been consumed) the polymer would be M_2 rich. To keep the ratios of the hypothetical polymerisation equal it would be necessary to feed in M_1 over the course of the polymerisation. There are also other more advanced methods used to predict the composition of co-polymers, including the *penultimate unit* model. In this model the unit *before* the terminal unit is also predicted to have an effect on the rate of addition of the monomers to the radical chain: this model has a further four possible reactions compared to the terminal

model and two more reactivity ratios. Usually the terminal model adequately describes the co-polymerisations of two monomers.

1.4.1.2 Graft Co-polymers

Graft co-polymers consist of a backbone of one type of monomer unit with pendant chains of a second monomer, as illustrated in figure (1.1)

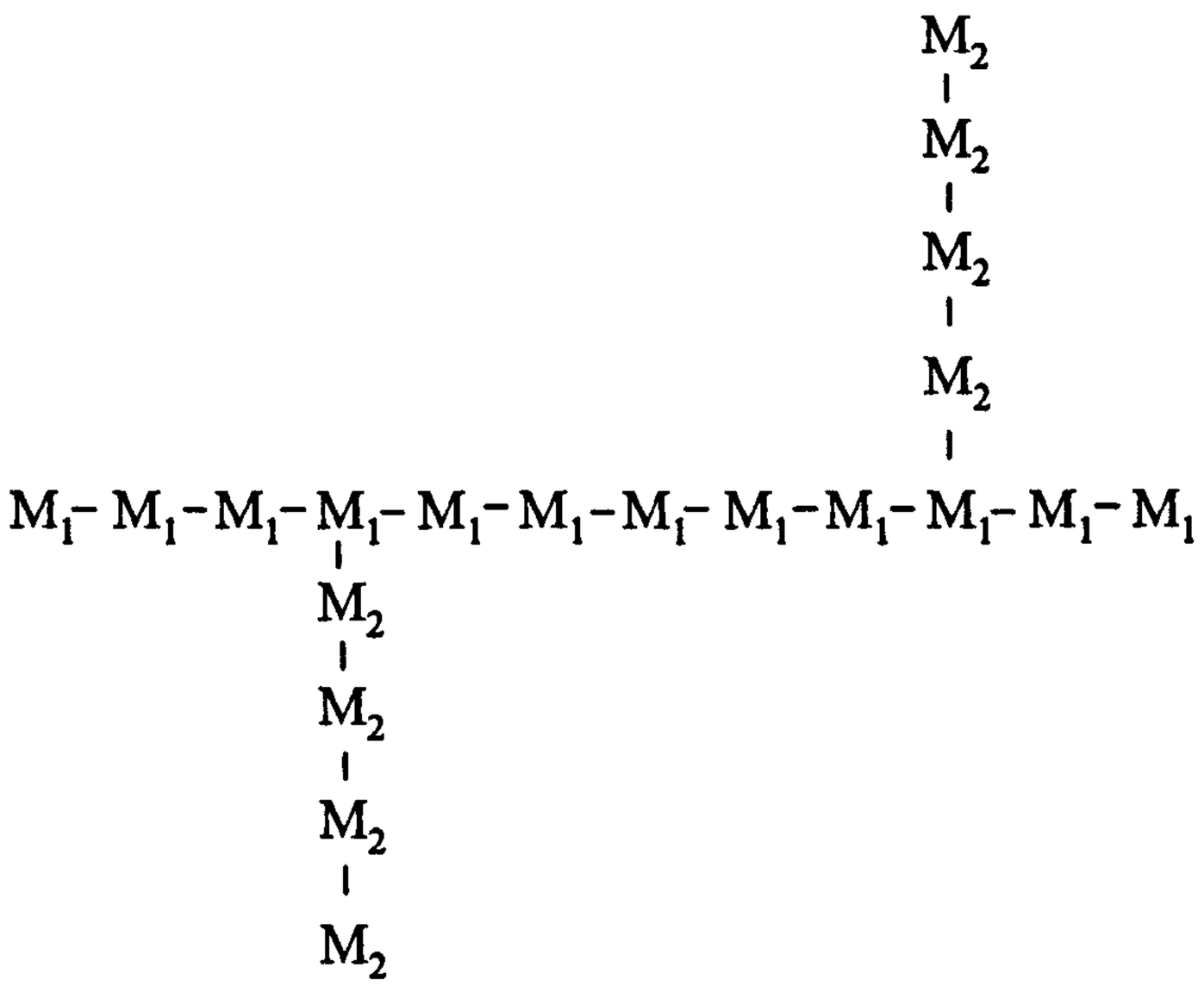
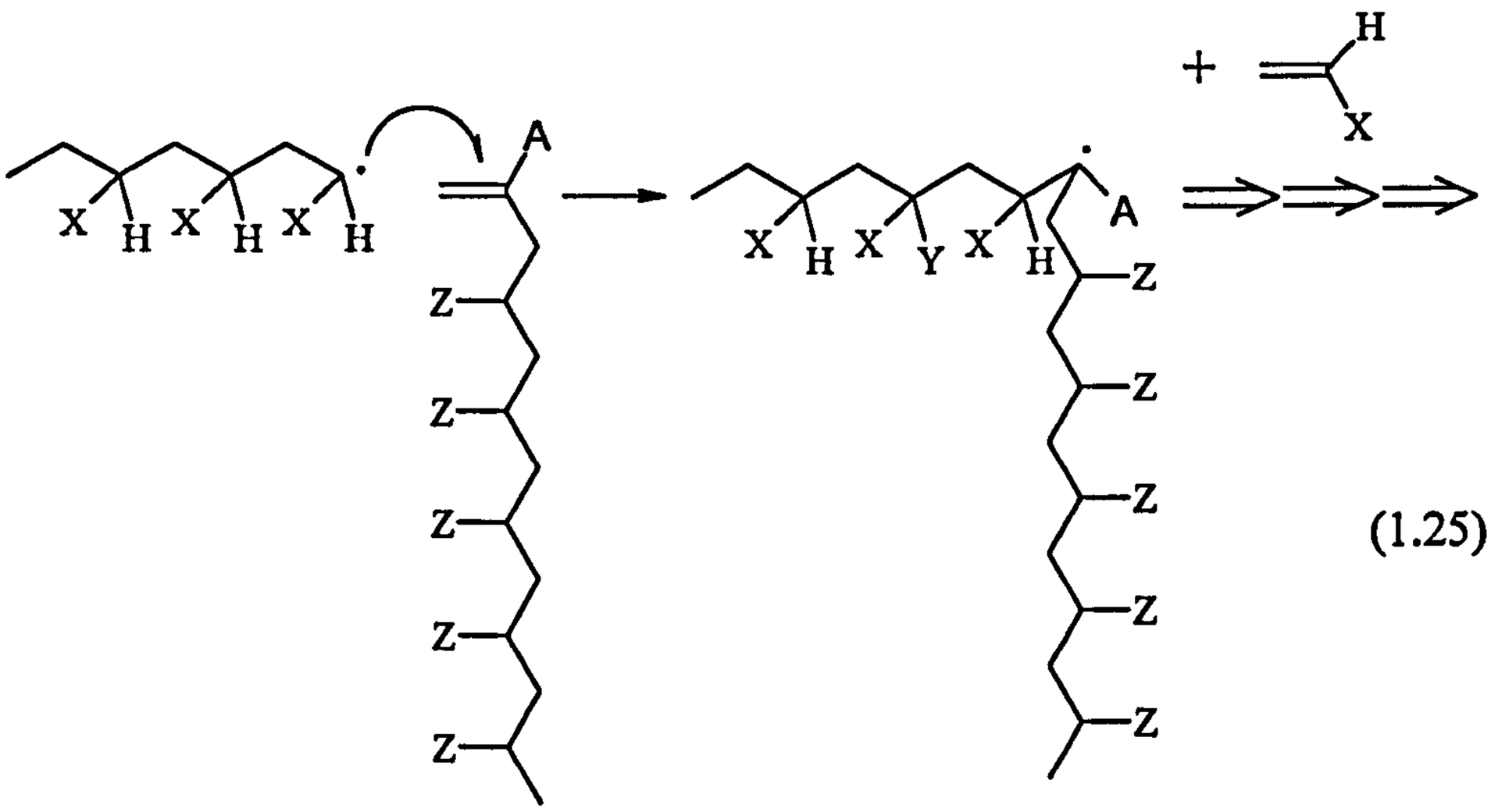


Figure 1.1 – *Structure of a graft co-polymer*

A graft co-polymer is usually much more difficult to prepare than a statistical co-polymer. Traditionally such polymer architectures are made by creating active sites along a polymer backbone, which initiate polymerisation of a second added monomer. Such active sites may be created by irradiating the polymer, but this technique will yield a number of side reactions. A much easier technique for the synthesis of graft co-polymers is the use of *macromonomers*[6-10]. Macromonomers are short-chained polymers that contain a terminal functional

group, which allows them to participate in further polymerisation reactions. Typically short polymer chains that are terminated by a vinyl group, which will be susceptible to radical attack, are used as macromonomers; hence such compounds may be simply added to radical polymerisations to give a graft co-polymer. An example of a possible reaction to incorporate a macromonomer into a polymer is shown in scheme 1.25.



(1.25)

The steric hindrance around the double bond will affect the monomers that can be used to make the backbone. It has been shown that if group 'A' is a methacrylate group then only unhindered monomers such as acrylates and styrene may be used to form graft co-polymers. If methacrylate is used as the co-monomer with a methacrylate terminated macromonomer then a β-scission reaction occurs (which will be described in section 1.5).

1.4.1.3 Block Co-polymers

Block co-polymers consist of a straight chain polymer with a 'block' of one monomer followed by a block of another (see figure 1.2)

$$M_1\text{–}\ M_1\text{–}M_1\text{–}M_1\text{–}\ M_1\text{–}\ M_1\text{–}M_2\text{–}\ M_2\text{–}M_2\text{–}M_2\text{–}\ M_2\text{–}\ M_2$$

Figure 1.2 – *Structure of a block co-polymer*

Commonly such compounds are made by 'living' polymerisation methods, where unlike in radical polymerisation, the rate of termination is very low i.e. $k_t \sim 0$. Using a living polymerisation technique it is possible to polymerise a monomer leaving an active group on the terminus of the chain which is capable of further polymerisation but not of termination; a second monomer is then added which polymerises, giving the block co-polymer (this is illustrated schematically in figure 1.26)

$$I^* + M_1 \longrightarrow IM_1^* \xrightarrow{M_1} \longrightarrow IM_1M_1M_1M_1^* \xrightarrow{M_2} \longrightarrow IM_1M_1M_1M_1M_2M_2M_2M_2 \qquad (1.26)$$

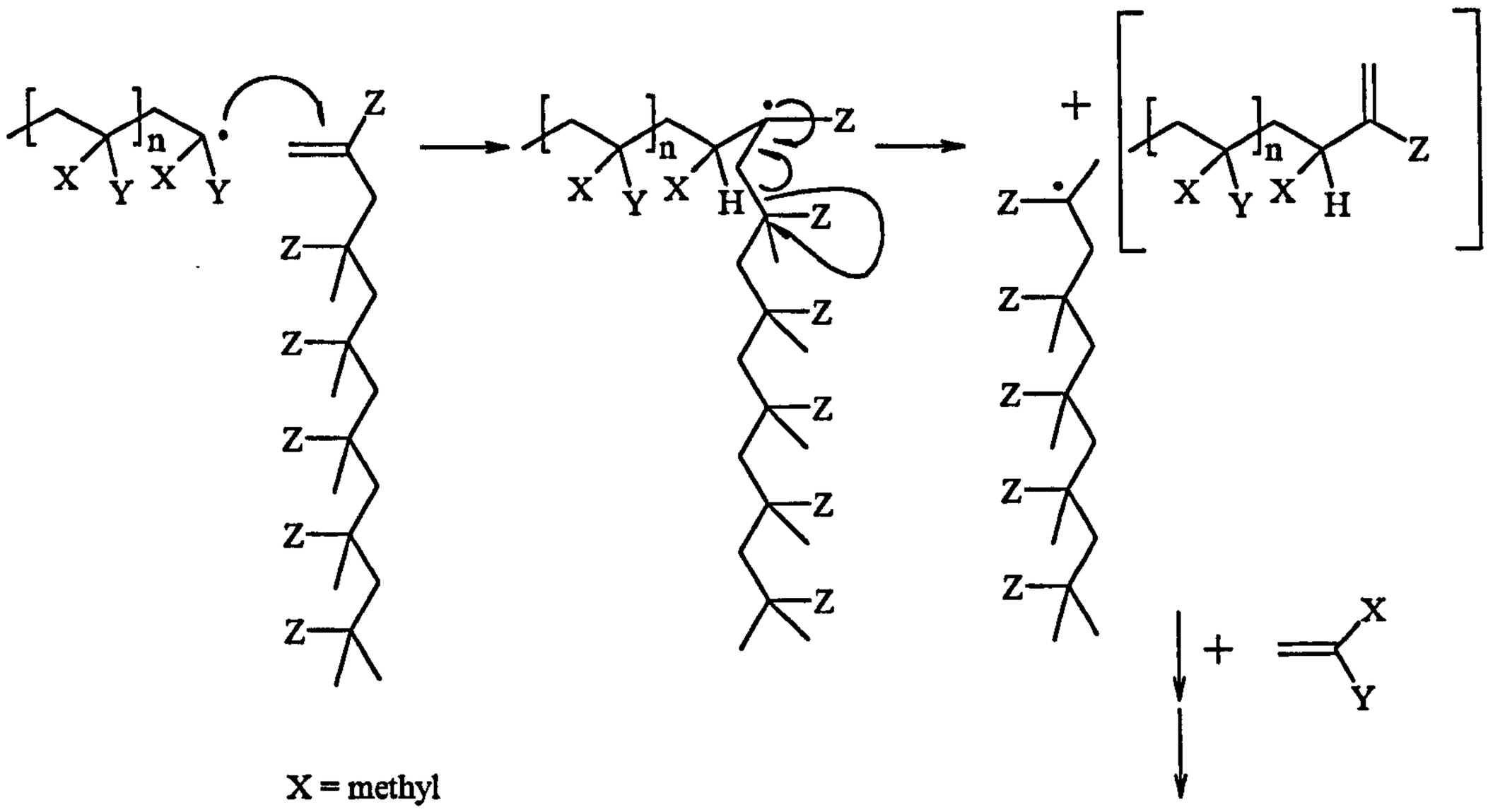
This type of reaction is usually initiated by an anionic or cationic species since neither carbocations nor carbanions are able to combine to terminate a polymerisation. Unfortunately such polymerisations are often difficult to carry out, since reagents need to be rigorously purified to remove contaminants which may terminate the polymer chain, also often the reagents react violently with water. Recently a technique known as 'living free radical' polymerisation has emerged which combines the undemanding conditions of radical polymerisation

with the possibility of synthesising block co-polymers[11-15]. Living radical polymerisation occurs by the reversible capping of a propagating radical chain, usually by a halogen atom. In the uncapped form the radical chains can propagate but in the capped form they are incapable of termination.

Another method for the synthesis of block co-polymers is *addition fragmentation chain transfer* and this will be discussed in the next section (1.5).

1.5 Addition Fragmentation Chain Transfer

It was mentioned in the previous section that it was possible to synthesise block co-polymers by the technique of addition fragmentation chain transfer. This technique involves the synthesis of one block of the co-polymer as a macromonomer (i.e. a terminally unsaturated polymer chain) and its subsequent reaction in a radical polymerisation to form the completed block co-polymer[16-20]. The terminally unsaturated polymer may be easily synthesised by using the technique of catalytic chain transfer (see section 1.7). If a methacrylate macromonomer is co-polymerised with a monomer that is not sterically hindered, such as an acrylate or styrene, then a normal co-polymerisation will occur with the macromonomer units being incorporated into the chain of the other monomer forming a graft co-polymer. If a more sterically hindered monomer such as a methacrylate is used as the co-monomer then a β – scission reaction occurs (see scheme 1.27) It can be seen that the reaction shown in scheme 1.27 is essentially a chain transfer reaction, the propagating polymer chain is stopped and a new polymer chain is initiated by the macromonomer radical formed.



X = methyl

Y = CO_2R

Z = CO_2R

R = alkyl group

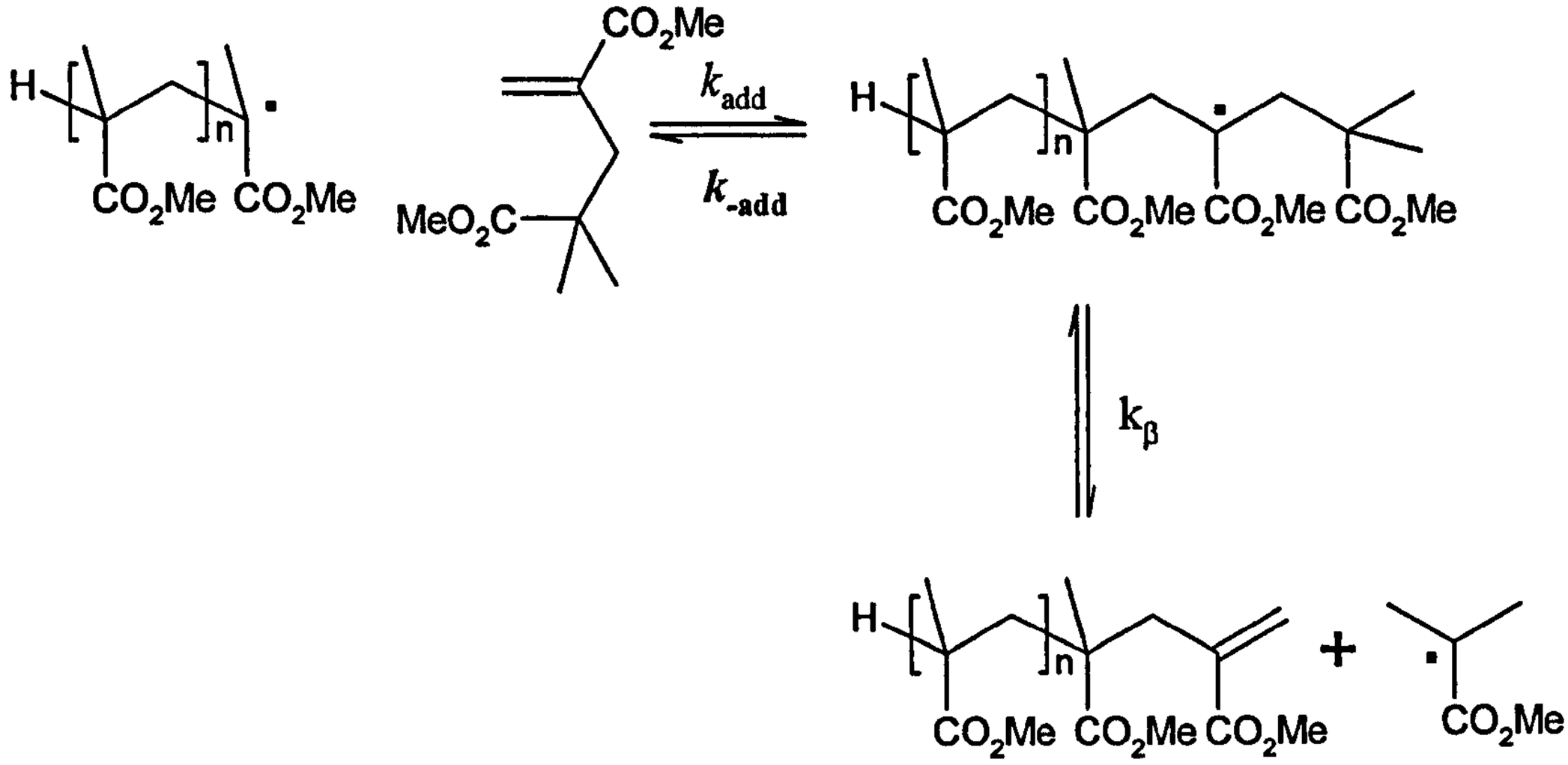
(1.27)

Although the reaction outlined is a chain transfer reaction, the chain transfer constant (Cs) of such compounds is quite low and so macromonomers are not usually used to reduce the molecular weight during a polymerisation but to introduce a different monomer type into the polymer chains. Chain transfer constants have been measured for MMA dimer, trimer, tetramer and macromonomer (Dp = 23)[19] and it was found that at 60 °C for MMA the following transfer constants were found:

MMA dimer: Cs = 0.013, MMA trimer: Cs = 0.19, MMA tetramer: Cs = 0.31 and MMA macromonomer: Cs = 0.21.

Dimer is thought to have a very low transfer constant due to the fact that the required leaving group is a relatively poor one and so the intermediate prefers to

break down to starting materials than to undergo the scission reaction (see scheme 1.28).



(1.28)

The method outlined in this section for synthesising block co-polymers is useful since the reaction is a radical one and is much more tolerant to trace impurities than conventional techniques such as anionic polymerisation.

1.6 Heterogeneous Polymerisation Techniques

The polymerisation of monomers in bulk (i.e. no added solvent) is not always convenient on an industrial scale since the reaction is often difficult to control and the high viscosity polymer produced will often be difficult to process. The addition of organic solvents will reduce the viscosity of the system but often there is the problem of residual volatile organic content (VOC) which is not considered to be very environmentally friendly. Commercially, polymers are often made by the heterogeneous techniques in aqueous media *emulsion* and

suspension polymerisation. These types of process involve the polymerisation of water insoluble monomers in an aqueous medium. Both suspension and emulsion polymerisation start as a rapidly stirred mixture of a water insoluble monomer and water. Small droplets of the monomer are formed which are dispersed through the aqueous phase. The difference between the two heterogeneous techniques lies in the locus of the polymerisation. In suspension polymerisation the main chain growth steps of polymerisation occur in the monomer droplets (~1-10 μm) giving a final particle size of around 1 μm or larger. In emulsion polymerisation the main chain growth occurs in a separate particle phase which is formed early on in the reaction. In emulsion polymerisation the final particle size is much smaller than in suspension with a typical particle size of the order of 100 nm.

1.6.1 Emulsion Polymerisation

Emulsion polymerisation[4,21,22] has distinct advantages over homogeneous bulk polymerisations. The polymer produced in the reaction can be easily taken to high molecular weight and also to high conversion in a short amount of time since the rate of reaction is much faster than the equivalent bulk reaction. The final product made in an emulsion polymerisation is in the form of polymer particles dispersed in water called a *latex*. The viscosity of this latex is not molecular weight dependent since the polymer is formed in discreet particles suspended in the aqueous phase and therefore the viscosity will be dependent on particle size and number. This means that high conversion, high molecular

weight polymers are much easier to process than with other methods of polymerisation.

1.6.1.1 Emulsion Polymerisation Mechanism

A typical emulsion polymerisation might consist of a stirred mixture of a water insoluble monomer, water and a surfactant. The surfactant is present to stabilise the polymer particles and prevent their aggregation. Since the mixture is being agitated, the majority of the monomer will consist of droplets dispersed through the aqueous phase but even with very hydrophobic monomers a small amount of the monomer will be present in the water phase.

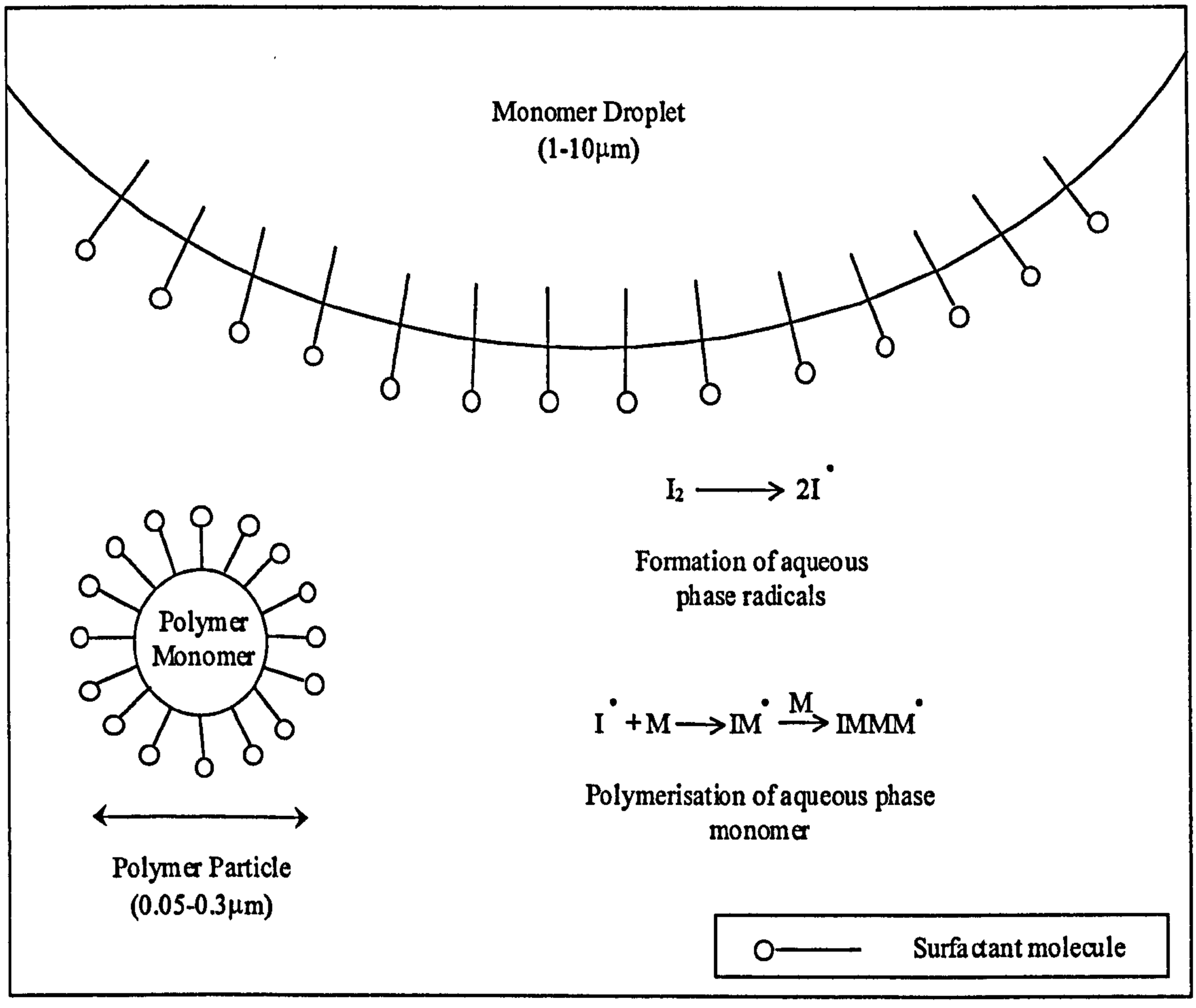


Figure 1.3 – *Emulsion Polymerisation*

On the addition of a *water* – soluble initiator, aqueous phase radicals are produced which will attack the monomer in the water phase. The aqueous phase monomer will begin to propagate (as in section 1.1.2). Once a few monomer units have been added to the initiator fragment the short chained (oligomeric) radicals will precipitate together to form a micelle. This process is called *homogeneous nucleation* and the number of monomer units that are necessary to induce precipitation depends on the solubility of the monomer used. The oligomeric radical can also enter a pre-formed micelle formed by the surfactant and this is called *micellar* nucleation. Both types of nucleation occur simultaneously and the extent to which one form predominates over the other depends upon the monomer solubility and the surfactant concentration.

The interior of the micelles contain a high concentration of monomer and the radical that has entered the micelle now begins to propagate forming polymer chains. The monomer consumed during the propagation steps is replenished by diffusion from the monomer droplets and so the micelles (now called polymer particles) will begin to swell. A particle containing a dead polymer will be formed by instantaneous termination when a new aqueous phase radical enters a particle containing a propagating radical. Alternatively the propagating radical chain can transfer to monomer giving a dead polymer chain and a monomeric radical which can then exit the particle.

In the description of emulsion polymerisations it is common to separate the emulsion into three phases, called intervals I, II and III, which often makes it easier to describe the mechanism of the process.

Interval I

In this part of the emulsion polymerisation particle nucleation is occurring. Generally this takes part in the first 10% of monomer conversion. Since the particles are still forming, there is an excess of surfactant in this period and so micelles are present during this interval. Both the number of particles and size of the particles present will be increasing in this part of the polymerisation.

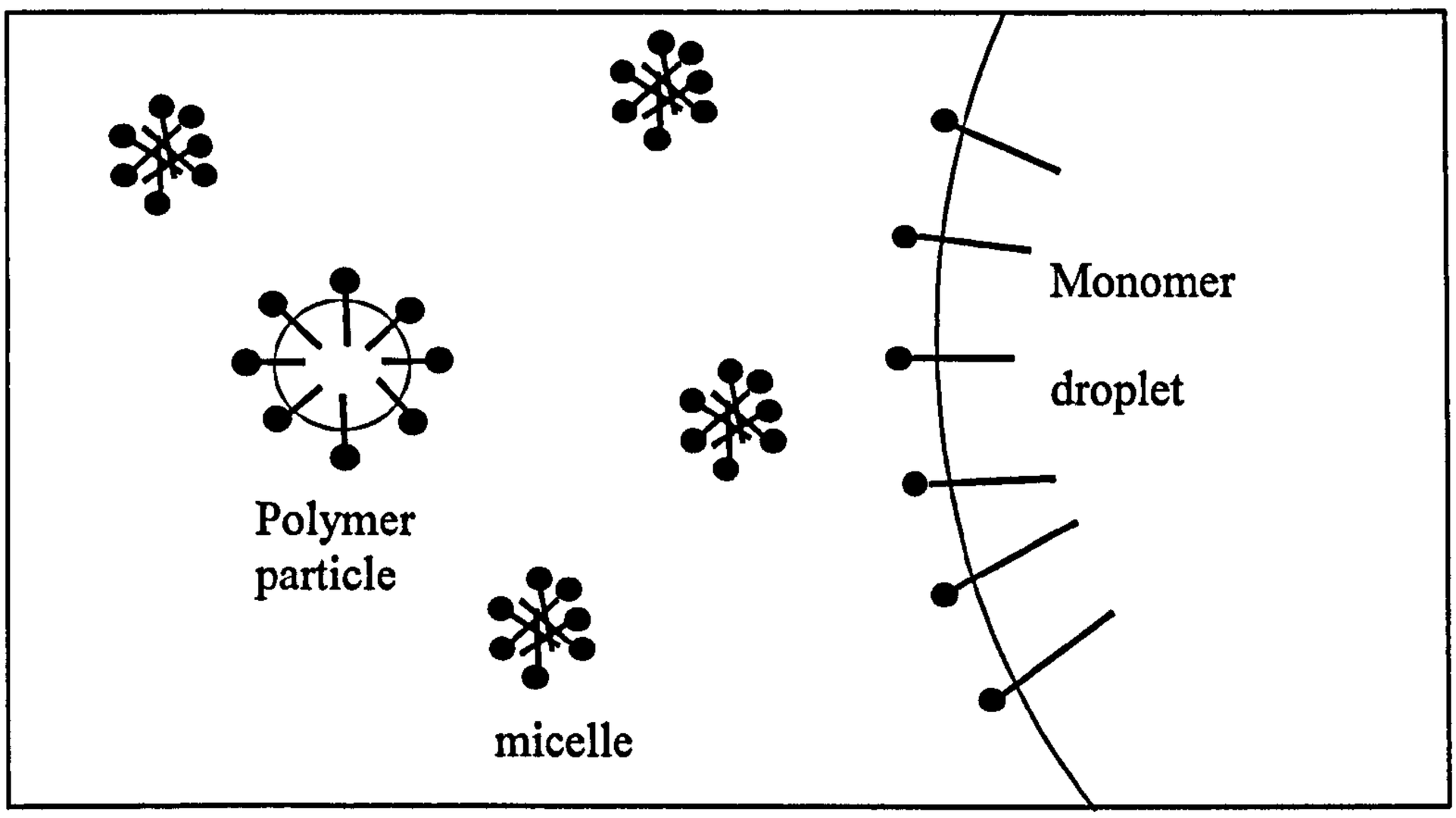


Figure 1.4 - *Interval I of an emulsion polymerisation*

Interval II

This is the particle growth part of the emulsion polymerisation and it is generally in the range 10-40% monomer conversion. The number of particles becomes constant and the particles expand in this stage drawing monomer from the droplets. Since the particles require more surfactant to stabilise them, due to their increase in size, the micelles present in interval I have disappeared.

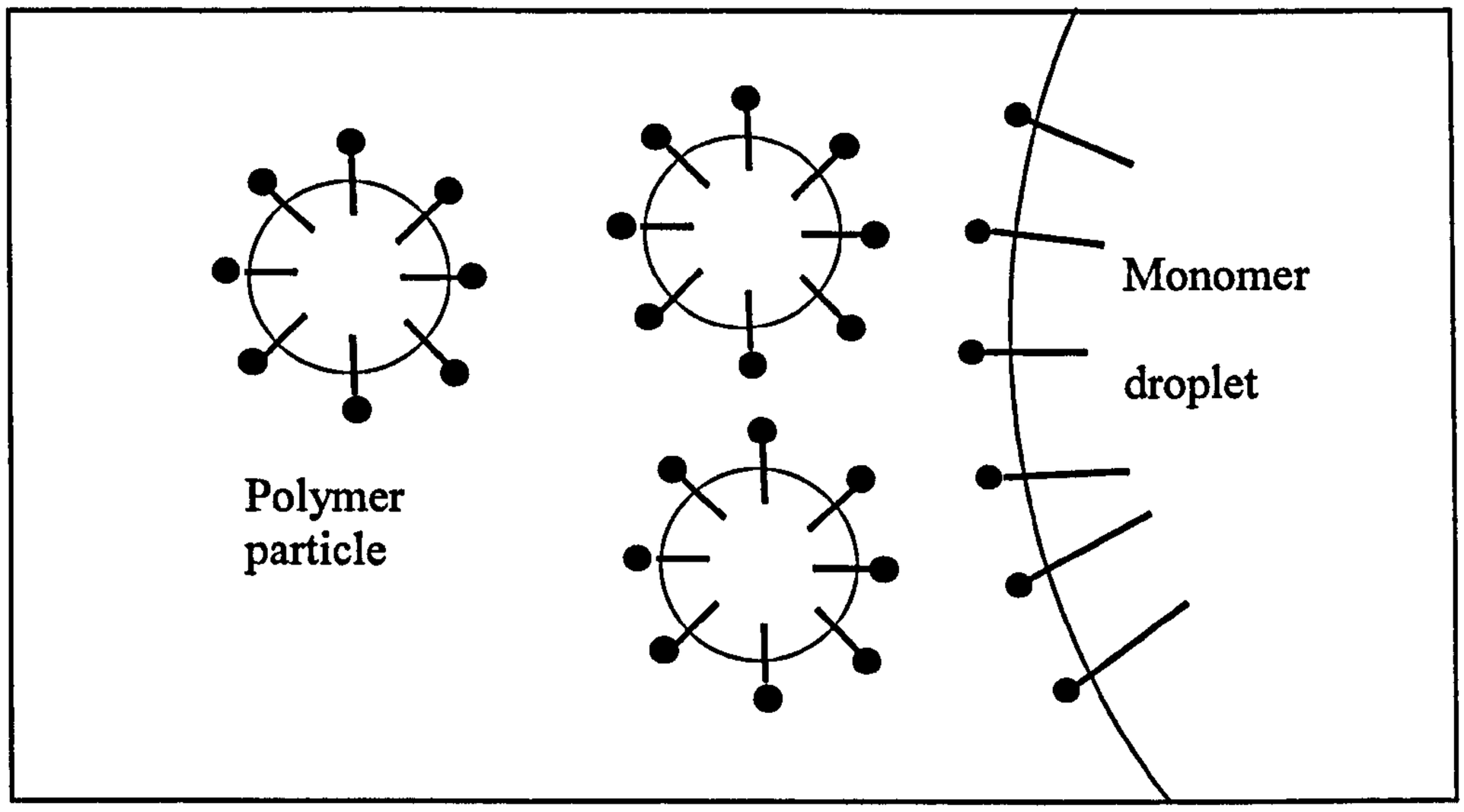


Figure 1.5 – *Interval II of an emulsion polymerisation*

Interval III

In interval III the monomer droplets have disappeared and the remaining monomer which is now present in the particles is converted to polymer.

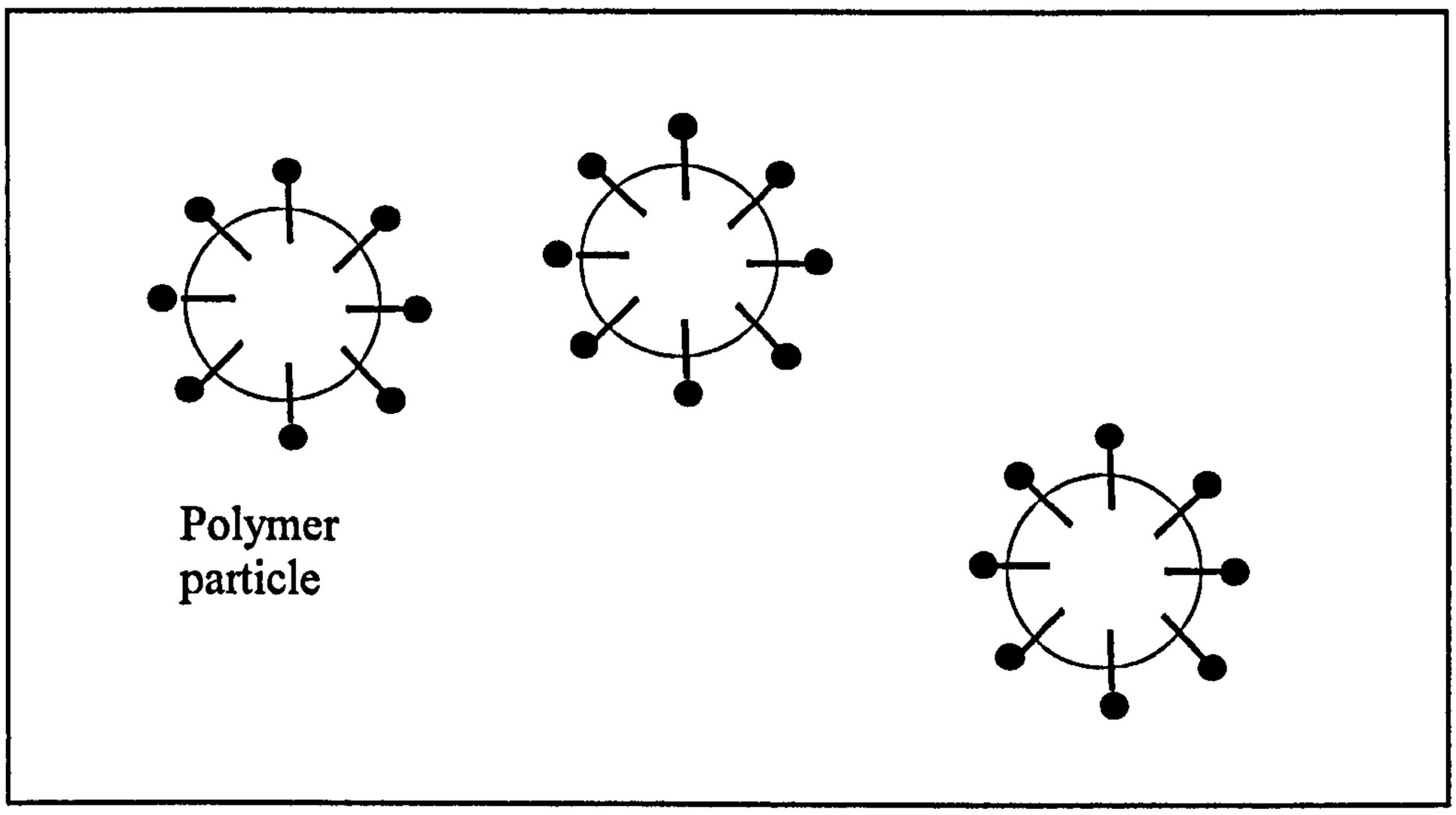


Figure 1.6 – *Interval III of an emulsion polymerisation*

1.7 Catalytic Chain Transfer

Catalytic chain transfer (CCT) polymerisation has emerged as a very convenient route to the synthesis of low molecular weight methacrylate based polymers[23-38]. It has been found that certain low spin cobalt (II) complexes have very high chain transfer constants (Cs values, section 1.1.3) several orders of magnitude better than traditional transfer agents such as mercaptans.

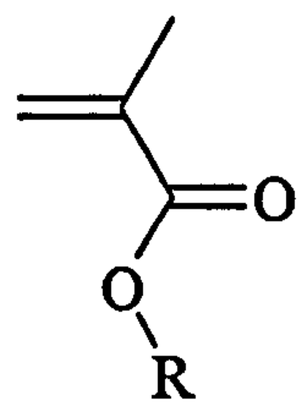
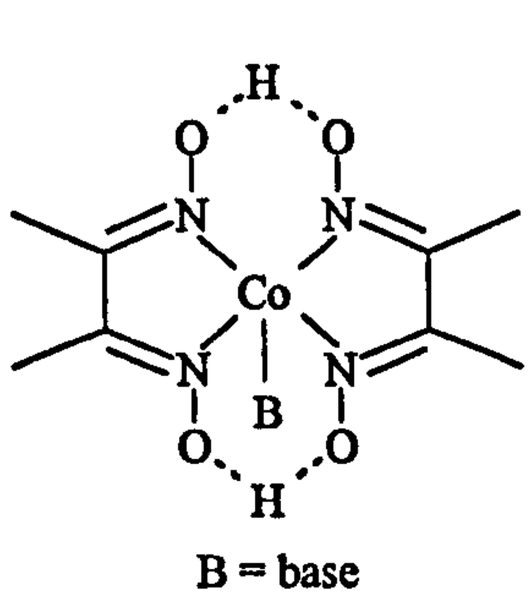


Figure 1.7 - *General structure of methacrylate type monomer used in CCT polymerisations*

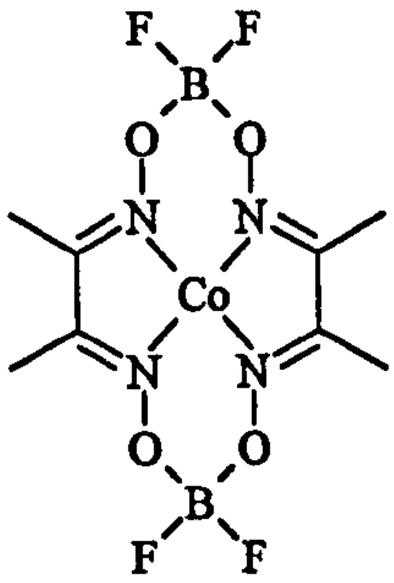
The result of the high transfer constant is that only very low amounts of CCT agent need to be employed in order to obtain very large reductions in molecular weight. Typically only parts per million levels of catalyst are required to synthesise oligomeric methacrylate polymers with less than twenty repeat units: in fact it is possible to synthesise methacrylate dimers and trimers using catalytic chain transfer polymerisation which would be difficult to synthesise by other methods. The low amount of catalyst that needs to be used results in low cost, but also there is the advantage that there will be low contamination of the final polymer product, which is a common problem for conventional transfer agents.

The first catalytic chain transfer agents to be used were cobalt porphyrin complexes [28,36,39,40] but these compounds had certain associated disadvantages namely in that they were highly coloured, possessed low solubility in organic media and were hydrolytically unstable. More commercially useful compounds, such as compound (1) have received much attention. It was found that a co-ordinating base ligand such as pyridine was necessary to improve the stability and oxygen sensitivity of the transfer agent[23]. The most widely used of the CCT agents is based on this structure with boron fluoride bridges giving the catalyst less oxygen sensitivity and more hydrolytic stability , this compound is commonly called COBF[41] (compound 2).



B = base

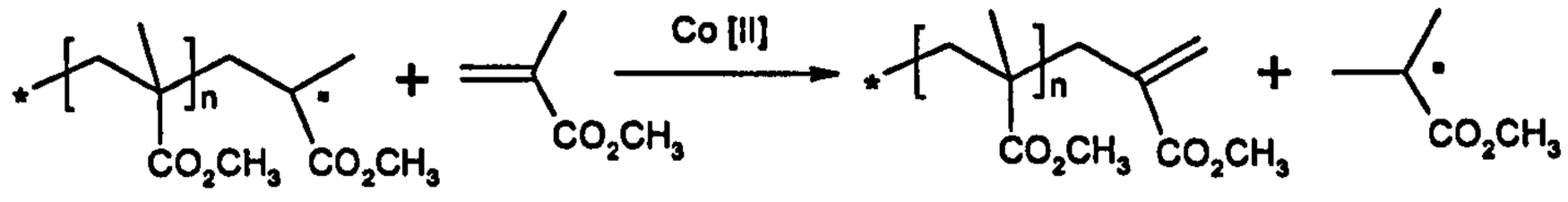
(1)



(2)

A polymer synthesised using the catalytic chain transfer method will be terminally unsaturated and this is the result of the removal of a β-hydrogen atom from the terminal methyl group of a propagating methacrylate polymer chain. Overall the catalytic chain transfer process can be summarised as the transfer of a hydrogen atom from a propagating polymer radical chain to a monomer molecule

catalysed by a Co (II) complex, this is illustrated in equation 1.29.



(1.29)

It is suggested that the hydrogen transfer reaction shown above occurs through a Co(III)- hydride intermediate and the Co(III) – hydrogen bond has been observed in this system[42,43]. A catalytic cycle (figure 1.8) has been postulated which involves a cobalt (III) -polymer adduct and the subsequent β hydrogen transfer[44]. There is no direct evidence for the existence of the cobalt – polymer adduct but there are examples in the literature of cobalt-carbon bonds being formed by radical combination[45]. The exact mechanism of the catalytic reaction has yet to be elucidated.

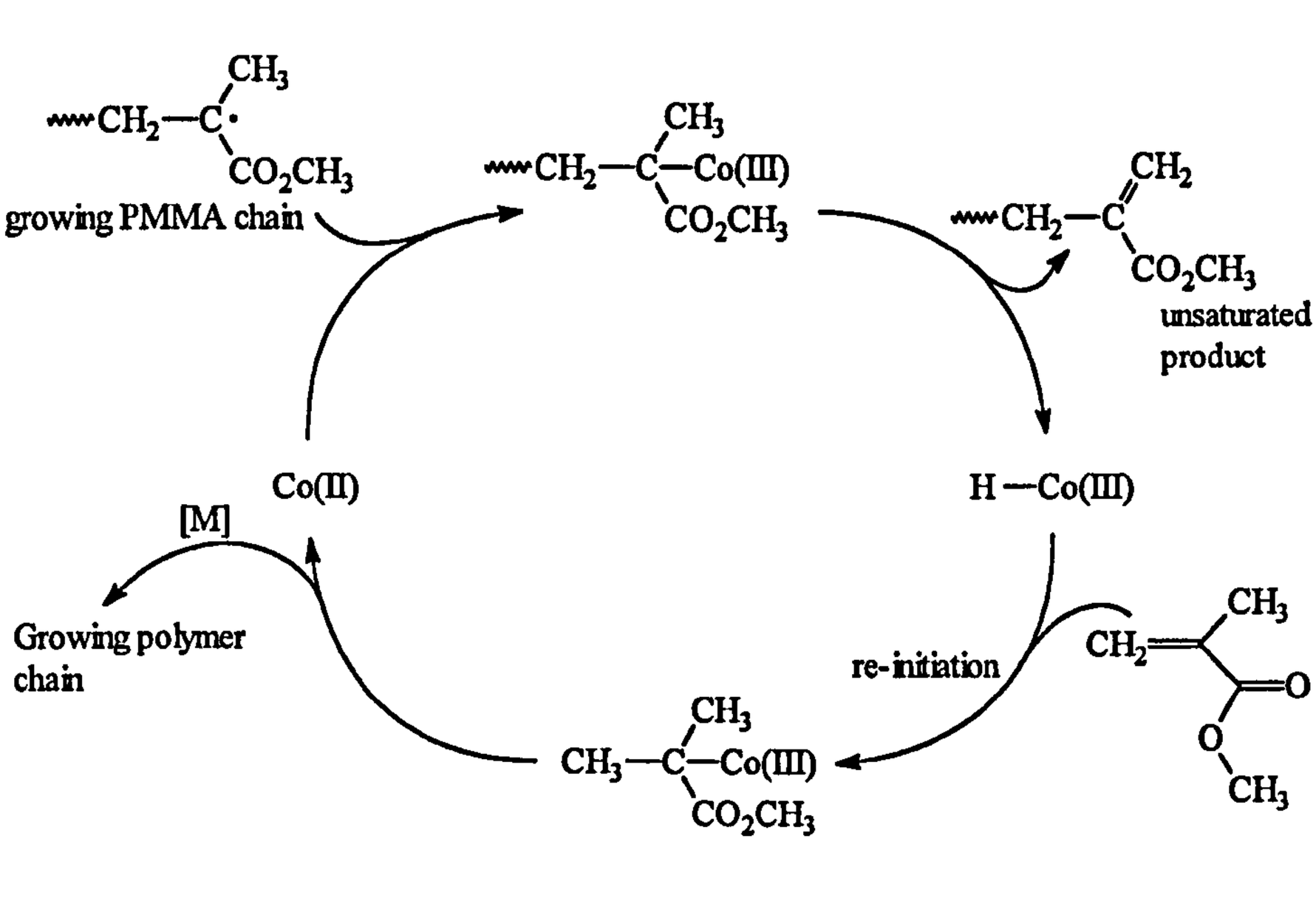
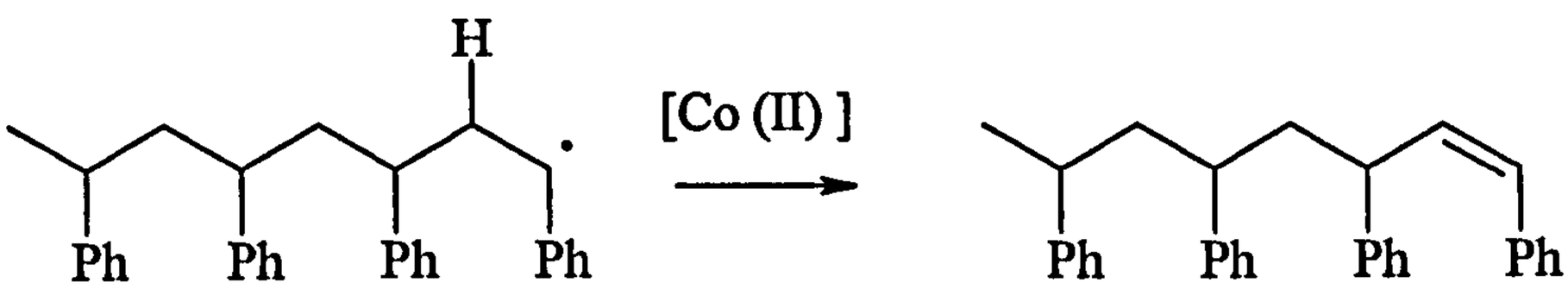


Figure 1.8 – *Proposed catalytic cycle for catalytic chain transfer reaction involving β – hydrogen transfer*

The macromonomers produced can be used in the synthesis of graft and block co-polymers (Sections 1.4.1.2 and 1.4.1.3) and so CCT can be used as the basis for the inexpensive synthesis of these types of polymers.

Unfortunately the catalytic chain transfer process does not work with all types of monomers. Styrenic macromonomers can be produced using CCT[46-49] but the activity of the catalysts is much lower than for the methacrylates due to the absence of a suitable β -hydrogen and the necessity of an in chain hydrogen abstraction[50] (equation 1.30).



(1.30)

The use of cobalt compounds in acrylate polymerisations has been shown to yield living type polymerisations instead of the CCT reaction[32,51].

It has been postulated that the catalytic chain transfer reaction for methacrylates is diffusion controlled (rather than chemically controlled) and this hypothesis is supported by experiments performed by Davis et al [52]. It was shown that if the CCT reaction were carried out in supercritical carbon dioxide then the transfer constant was very much enhanced. Supercritical fluids have liquid like densities but only gas like viscosity and the increase in Cs was thought to be due to the higher rate of diffusion in the system. In other work by Davis et al[53] it was shown that the opposite effect was observed when a very viscous methacrylate monomer was used (2-phenoxyethyl methacrylate) with a much lower Cs being observed in this system compared to in a methyl methacrylate polymerisation.

The use of Co(III) compounds as CCT agents has also been described[54-56] where one of the axial ligands is an alkyl group. The CCT reaction of Co(III) is thought to proceed by the homolysis of the Co-alkyl bond yielding a Co(II) species able to undergo the CCT reaction.

As was stated previously, the CCT polymerisation of methacrylate monomers yields a polymer with a terminal vinyl group (figure 1.9). MMA macromonomers have been shown not to undergo homo-polymerisation[10,57] but they may be used in co-polymerisations in order to synthesise graft and block co-polymers (sections 1.4.1.2 and 1.5 respectively).

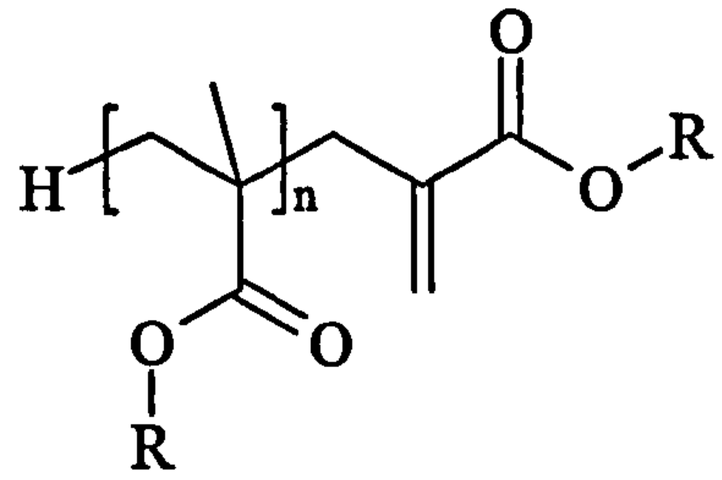


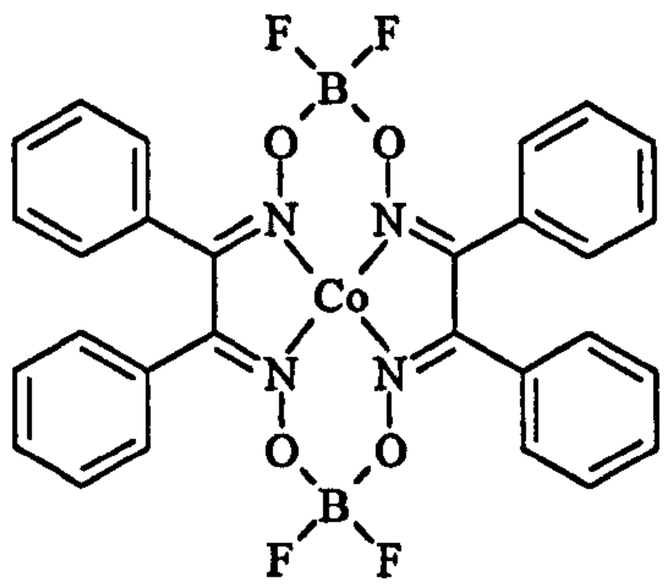
Figure 1.9 – *Structure of methacrylate macromonomer synthesised by CCT*

1.7.1 Catalytic Chain Transfer Emulsion Polymerisation

It has been previously shown that catalytic chain transfer may be performed under emulsion polymerisation conditions[58-63]. High conversion, low molecular weight methyl methacrylate polymers were prepared simply and quickly by performing the CCT process in emulsion using the chain transfer

agent COBF and the results published showed that this was a very effective technique for synthesising methacrylate macromonomers. It was shown that in order to produce a stable latex and for effective chain transfer to be observed, a feed of catalyst/monomer mixture into the aqueous phase had to be performed.

For the catalytic chain transfer agent COBF it was determined that the catalyst partitions between the MMA monomer and aqueous phases such that $[COBF]_{MMA}/[COBF]_{aq} = 0.68$ [58]. The COBF is therefore roughly equally soluble in the MMA and water phase. It has been shown that the catalyst must be reasonably soluble in both phases for the emulsion polymerisation to work effectively. The partitioning studies on the catalyst COPhBF (compound 3) in an MMA / water mixture, show that the catalyst resides almost exclusively in the monomer phase [59].



(3)

It was found by Kukulj et al that when the chain transfer catalyst CoPhBF was used in the emulsion polymerisation of MMA that the activity of the catalyst was significantly reduced compared to COBF [59]. It is postulated that the catalyst must be sufficiently soluble in the aqueous phase to facilitate transfer of the catalyst between the monomer droplets and the particles (and between different particles) in order for efficient CCT emulsion polymerisation to occur.

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Chapter 2

The Catalytic Chain Transfer Emulsion Polymerisation of Alkyl Methacrylate Monomers

2.1 Introduction

The facile synthesis of macromonomers using catalytic chain transfer in emulsion polymerisation was reviewed in Chapter 1. It was shown that methacrylate monomers underwent very efficient chain transfer with certain cobalt complexes. Tiny amounts of the cobalt compounds added to a polymerisation achieve large reductions in molecular weight due to the catalytic nature of the transfer process. Emulsion polymerisation was also shown to be an industrially important process due to the fact that high conversion polymers can be synthesised easily and quickly. Catalytic chain transfer has been shown to be an effective technique for the synthesis of functional oligomers under emulsion polymerisation conditions[1-6]. The results published by Suddaby et al.[1] show that the activity of the catalytic chain transfer agent is an order of magnitude less than in an equivalent bulk polymerisation. The loss of catalytic activity was thought to be due to destruction of the catalyst by the acidic initiator and the fact that some of the catalyst will not be present at the locus of polymerisation (the polymer particles)

Other results shown by Suddaby indicate that there is a threshold level of catalyst necessary for efficient oligomer synthesis to occur. If the catalyst concentration is below this level it was shown that the catalytic activity is severely reduced. The reduction in catalytic activity was thought to be due to an increase in rate of polymerisation at low catalyst levels. The higher rate of polymerisation would result in a lower amount of monomer in the polymer particles, which would raise the glass transition temperature. It was thought that the glass transition temperature was higher than the reaction temperature at low catalyst concentrations, which restricted the movement of the catalyst about the system resulting in a low observed catalytic activity.

This chapter aims to expand on the already published data and to further study the system to determine if a greater range of catalyst concentrations may be employed and hence a greater range of methacrylate macromonomers be produced.

2.2 The *CCT* Emulsion Polymerisation of Methyl Methacrylate

The reactions shown in table 2.1 were carried out using identical conditions to those used by Suddaby et al[1]. The catalyst was dissolved in 200 mL of monomer and fed into 450 mL of water over the period of one hour. The initiator used was the water soluble 4,4' azobis (4-cyanovaleric acid) and the polymer particles were stabilised using an aerosol type surfactant. The target polymer compound is shown in figure 2.1.

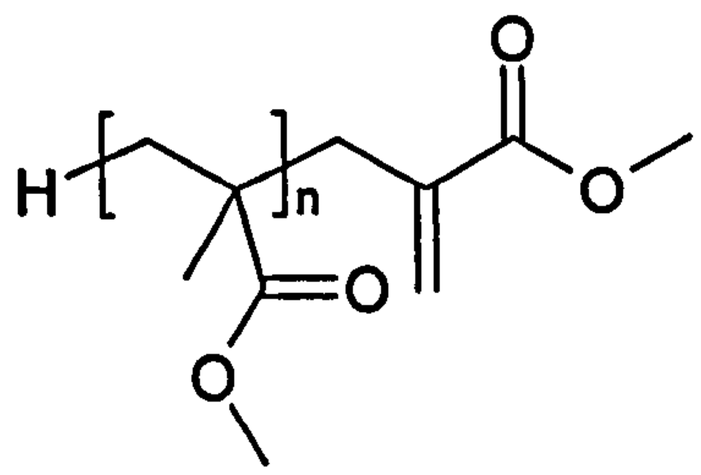

Figure 2.1 – Structure of PMMA macromonomer

Reaction	Wt. COBF (g)	Ppm COBF	Feed Conditions	Mn	PDi	Inst. Conv.	Cs^E
M1	0.0300	35.75	100% fed	2120	1.65	1.003	1320
M2	0.0210	25.03	100% fed	3260	1.77	1.012	1226
M3	0.0156	18.59	100% fed	4030	1.91	1.015	1337
M4	0.0139	16.56	100% fed	4160	1.90	0.977	1451
M5	0.0122	14.53	100% fed	10500	3.91	1.033	653
M6	0.0000	0.00	100% fed	116000	2.61	1.001	-

Table 2.1 – *End properties of MMA emulsion polymerisations*

The NMR of the product from reaction M2 clearly shows the vinyl peaks associated with the terminal unsaturation of this polymer. The peak corresponding to the methoxy group in MMA is found at 3.75 ppm, the fact that it is not present in the NMR of the PMMA polymer means that there is no unreacted monomer in the sample.

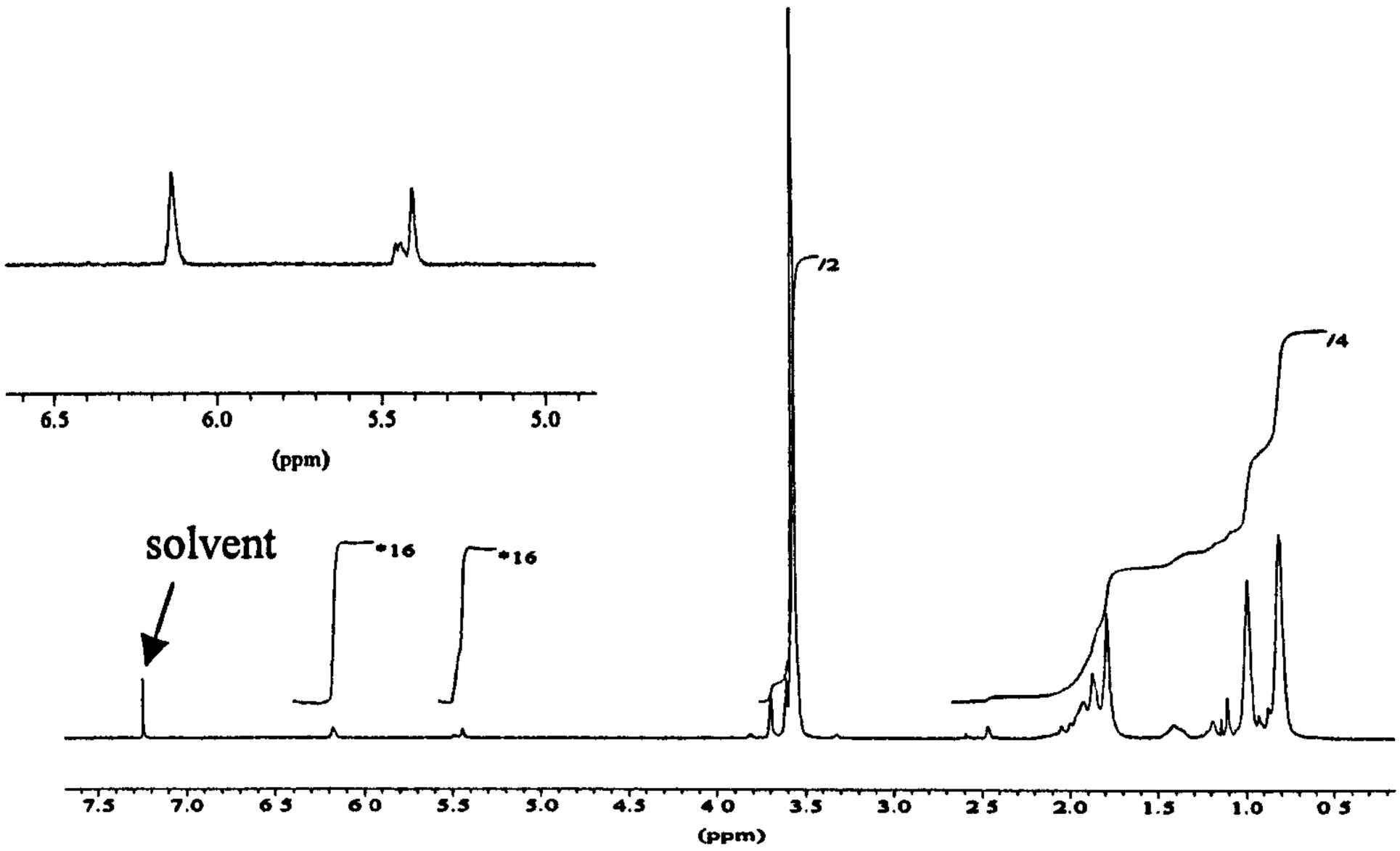

Figure 2.2 – ^{1}H NMR spectrum in $CDCl_3$ of PMMA made by CCT in emulsion

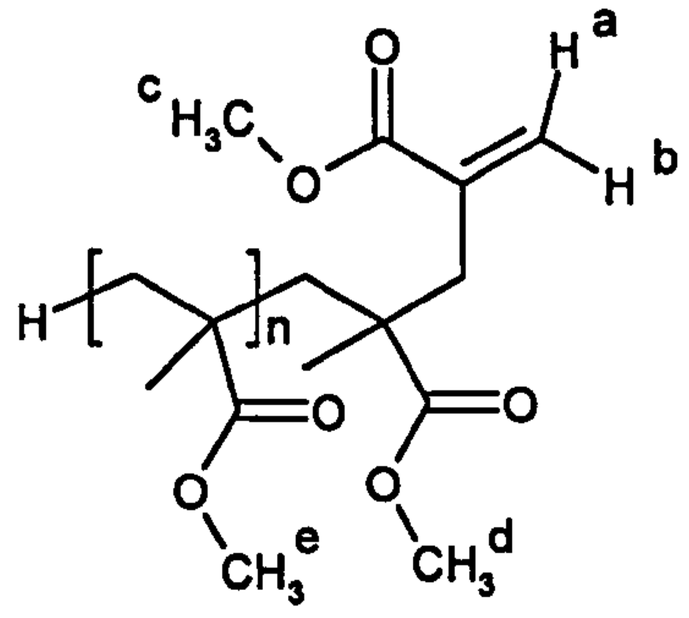

Figure 2.3 – *Structure of PMMA with protons labelled for NMR analysis*

Peak (ppm)	Integral	Multiplet Type	Assignment
6.10	1.00	(s)	Vinyl peak [a]
5.44	0.98	(s)	Vinyl peak [b]
3.67	90.48	(s)	Terminal methoxy [c]
3.58		(s)	First in chain methoxy [d] nearest vinyl
3.53		(s)	Methoxy in chain [e]
0.5 – 2.5	155.90	(m)	In chain CH_2 and CH_3 protons

Table 2.2 – *NMR results for figure 2.2*

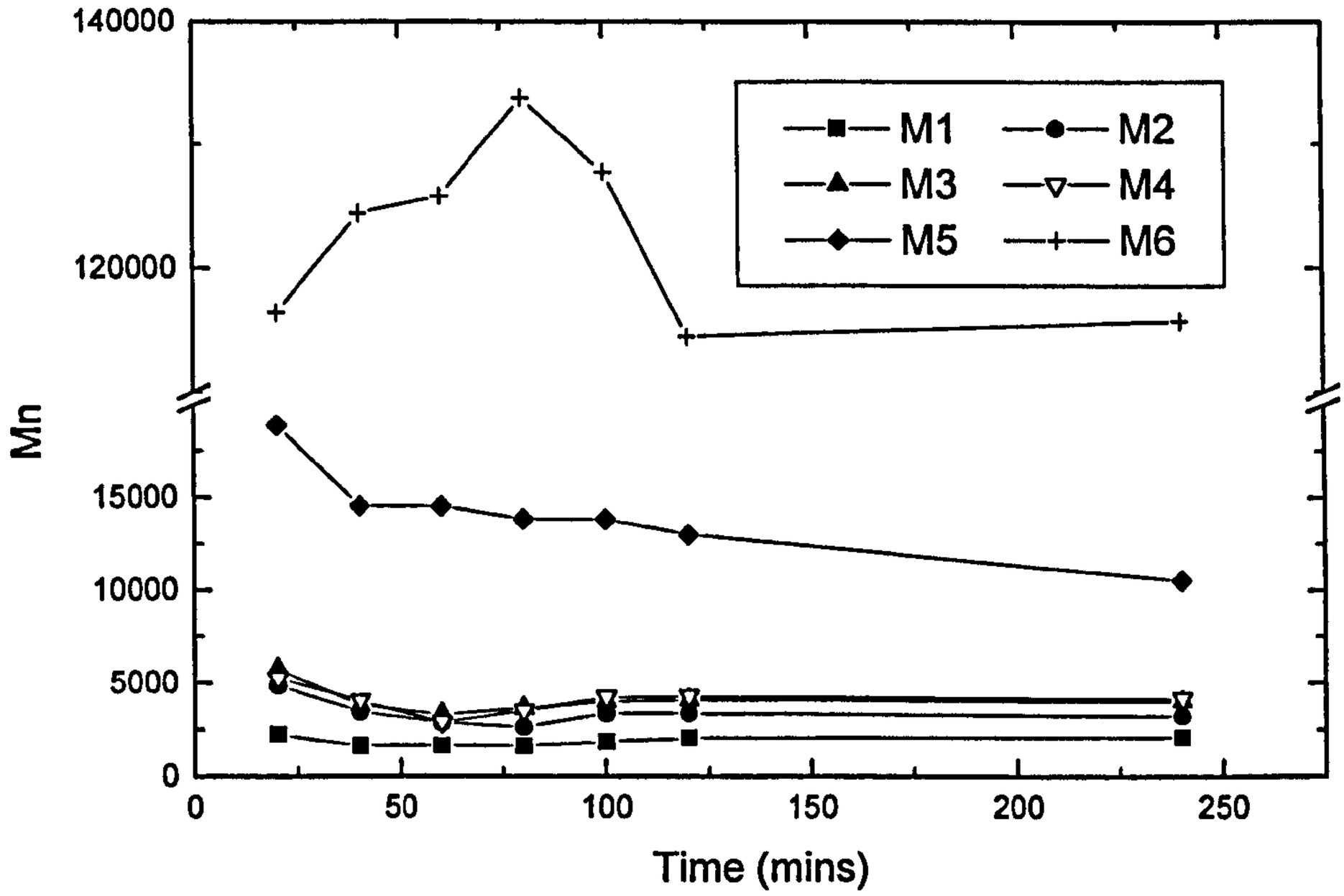

Figure 2.4 -*Time versus M_n graph for emulsion polymerisations M1-M6*

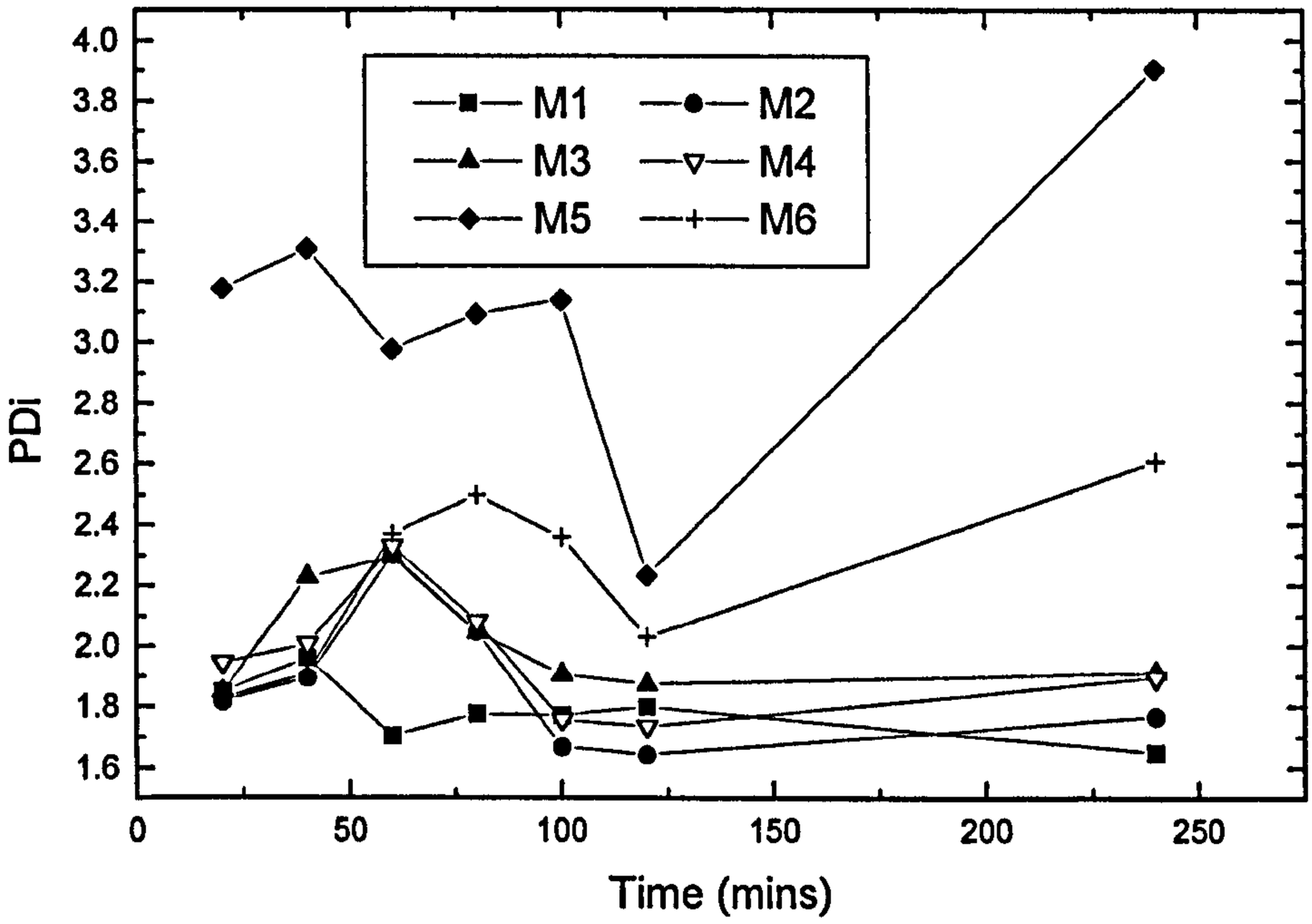

Figure 2.5 - *Time versus polydispersity index graph for emulsion polymerisations M1-M6*

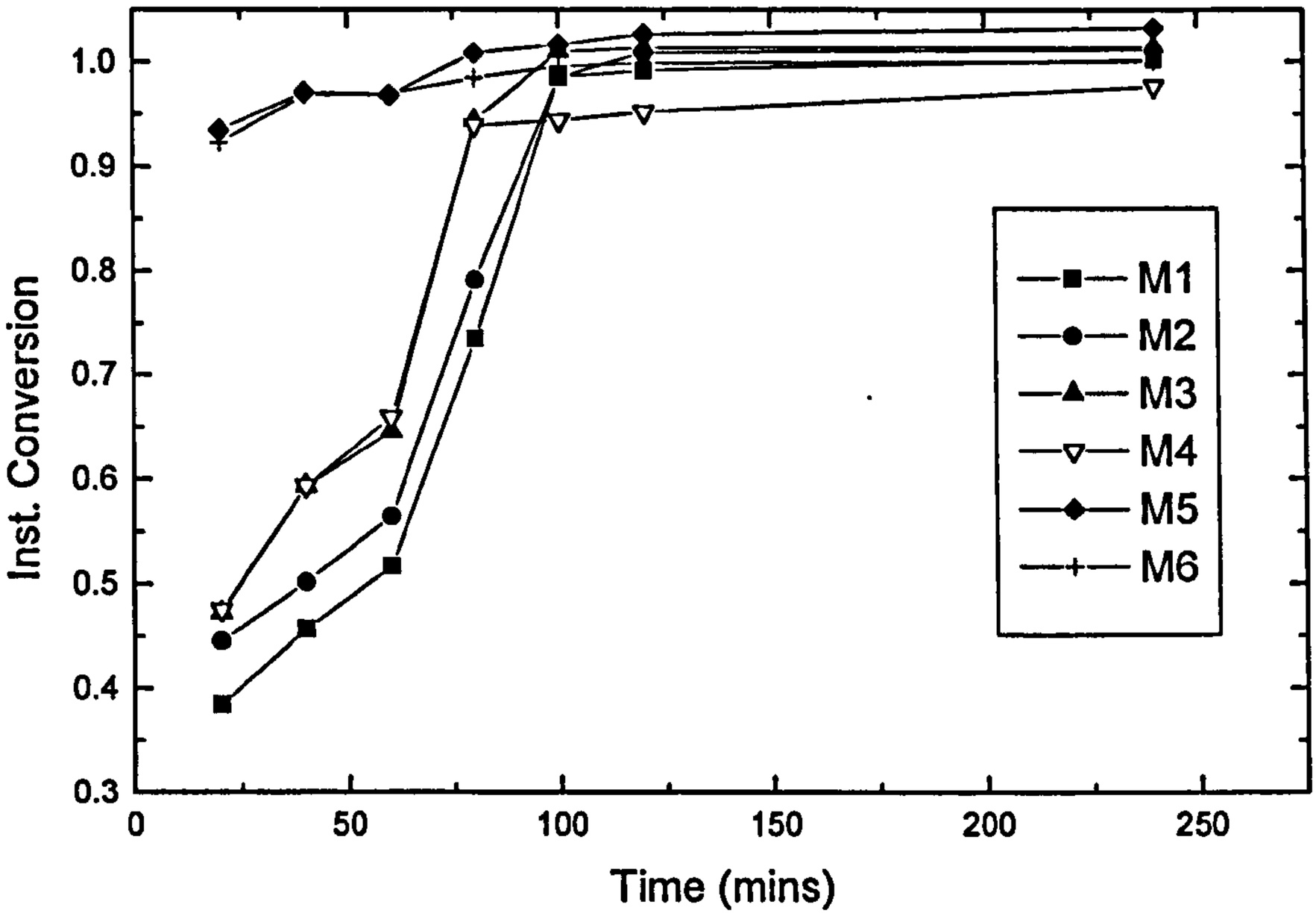

Figure 2.6 - *Time versus Instantaneous Conversion graph for emulsion polymerisations M1-M6*

The data shown in table 2.1 and graphically in figures 2.4 - 2.6 are in good agreement with that published by Suddaby et al[1]. The reactions M1-M4 show good reduction in molecular weight compared to the control reaction M6 and the polydispersity is low throughout the polymerisation for these reactions. All polymerisations where effective CCT is observed (M1-M4) show a reduction in molecular weight over the period of the feed time (the first 60 minutes). The decrease in molecular weight is due to an effective increase in the concentration of CCT agent in the particles during this time. After the first hour the molecular weight increases, possibly due to catalyst destruction by the acidic initiator. The instantaneous conversions for reactions M1-M4 are low through the first hour of the reaction showing that the polymerisations are under non-starved fed

conditions and the conversion rises close to 100% conversion after the end of the feed time illustrating the speed of the reaction. In the absence of chain transfer agent (polymerisation M6) the reaction runs much faster than when the catalyst is present, with the reaction being above 90% instantaneous conversion throughout the reaction, indicating that the polymerisation is under starved fed conditions. The termination of a radical polymerisation is usually diffusion controlled and so the length of the polymer chain (at low molecular weights) will affect the rate of termination. If the rate of termination is increased, then the rate of polymerisation will be decreased and so for CCT reactions the rate of polymerisation will be slower than for an equivalent control reaction with the absence of CCT agent.

Figures 2.4 - 2.6 show that polymerisation M5 exhibited different behaviour to the other reactions. The molecular weight of the polymer produced was higher than expected (due to a much lower Cs^E value), the polydispersity was much higher than normal and the instantaneous conversion versus time plot showed that the rate of reaction was much faster than for reactions M1-M4. These findings are consistent with those found by Suddaby et al and the differences were attributed to the fact that the glass transition temperature of the polymer/monomer mixture in the particles was higher than the reaction temperature for the reaction. The resultant glassy polymer particles were thought to restrict the movement of the catalyst and result in the observed reduction in chain transfer constant. The consequence of these observations is that it would not be possible to synthesise macromonomers with a molecular weight of above 3000 g mol^{-1} using the standard one hour feed of the monomer.

Since for reaction M5 the polymerisation was under starved fed conditions it was postulated that an injection of a shot of the monomer/catalyst mixture at the start of the polymerisation would act to bring the polymerisation to a non - starved fed state. Early on in the polymerisation inside the particles there would be an excess of monomer which would bring down the glass transition temperature of the polymer and hence allow free movement of the catalyst molecules.

Reaction	Wt. COBF (g)	Ppm COBF	Feed Conditions	Mn	PDi	Inst. Conv.	Cs^E
M7	0.0150	17.87	20%shot/ 80% fed	4230	1.79	0.923	1322
M8	0.0087	10.37	20%shot/ 80% fed	7940	1.80	0.969	1215

Table 2.3 – *End conditions for polymerisations M7 and M8*

The results shown in table 2.3 above show that the shot of monomer at the start of the reaction has been successful in improving the activity of the chain transfer agent COBF in these emulsion polymerisations. The effective chain transfer constants in emulsion (Cs^E) are close to the values for polymerisations M1-M4.

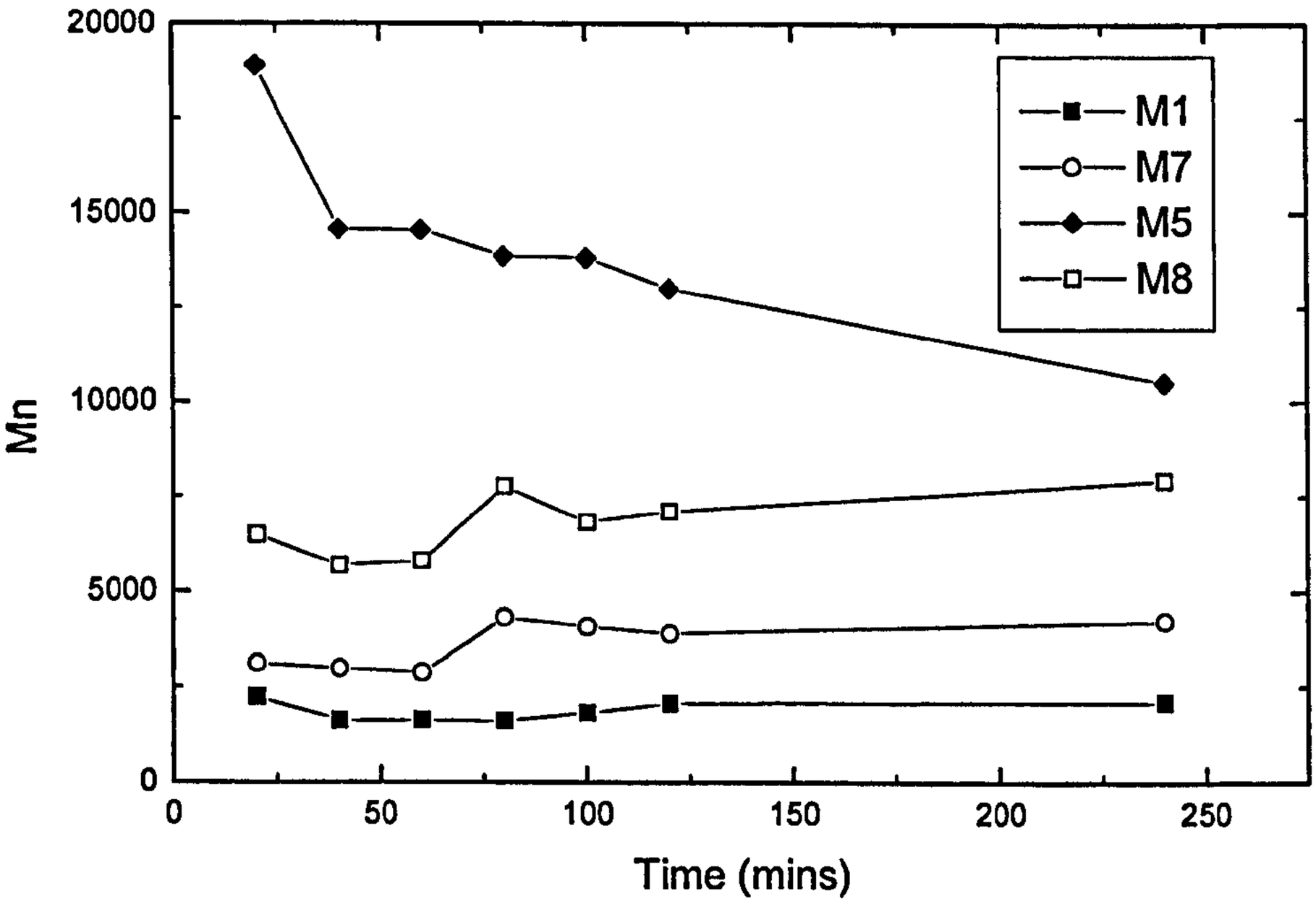

Figure 2.7 – *M_n versus time graph for polymerisations M1, M5, M7 and M8*

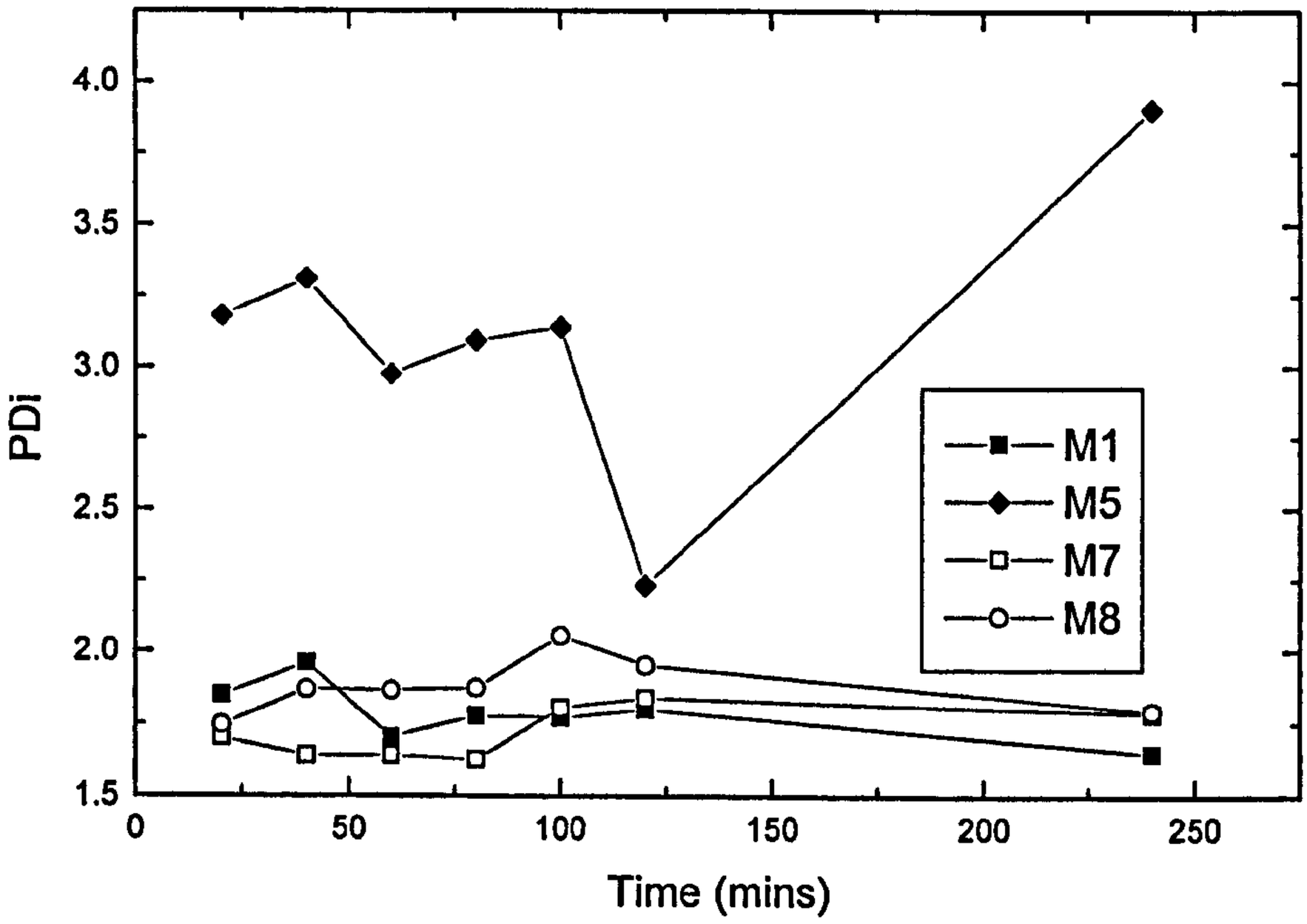

Figure 2.8 – *Polydispersity index versus time graph for polymerisations M1, M5, M7 and M8*

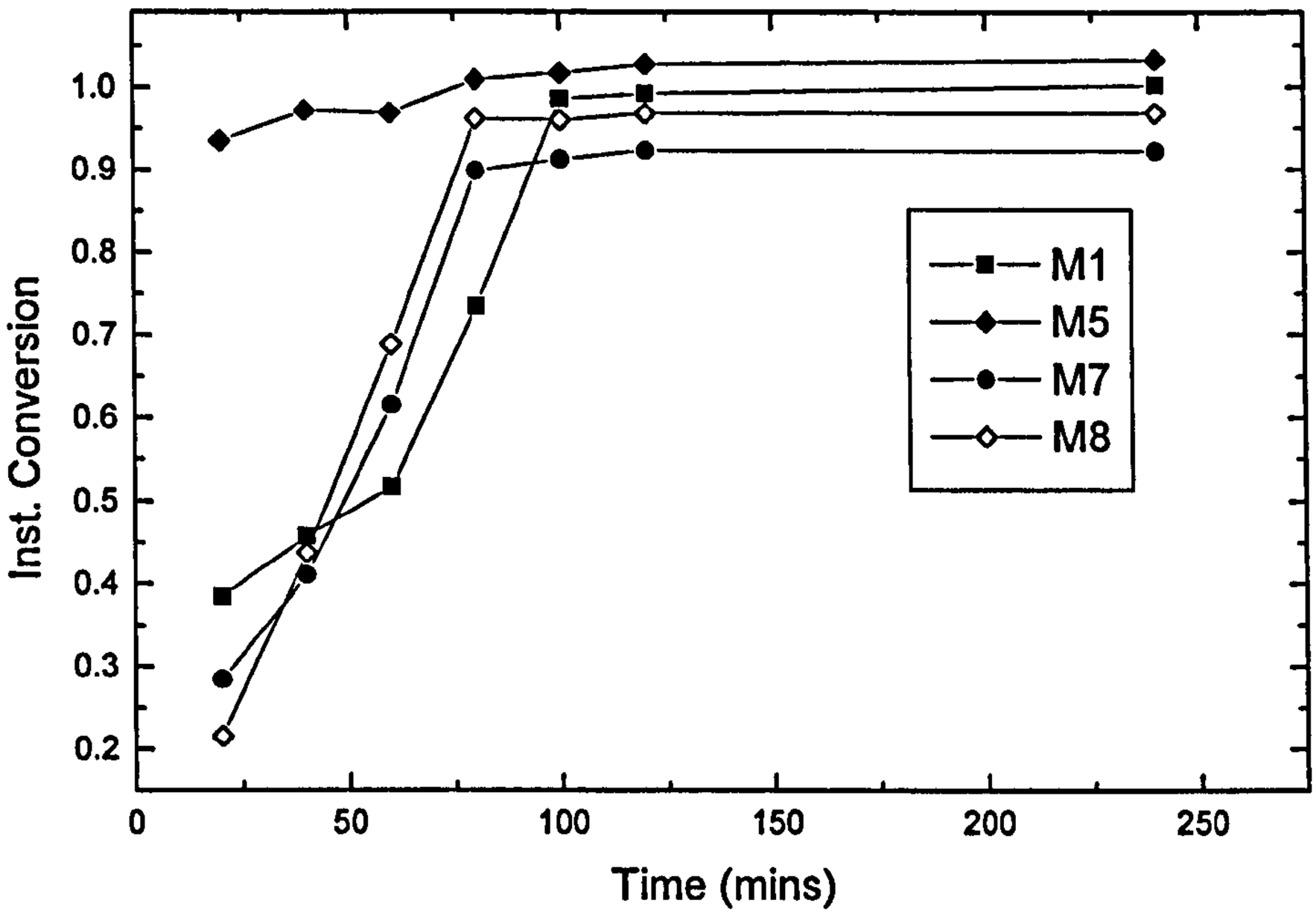

Figure 2.9 – *Instantaneous conversion versus time graph for polymerisations M1, M5, M7 and M8*

As can be seen in graphs 2.7 and 2.8 the shot of monomer at the start of the reaction has been successful in improving the CCT efficiency, both the M_n and PDi are in the range that would be expected for efficient transfer activity. The results from experiment M6 (which has a catalyst level close to that of experiment M4) shows that the monomer shot at the start of the experiment does not adversely effect the polymerisation when efficient CCT is already observed. The instantaneous conversion versus time graph in figure 2.8 shows that the addition of the monomer shot at the start of reaction M7 brings the polymerisation from starved fed to non-starved fed conditions as predicted. The results indicate that for efficient CCT to occur the rate of polymerisation must be sufficiently slowed so as to give starved fed conditions. Under these conditions

monomer is present in the particles which means for an MMA polymerisation that the particles will be rubbery rather than glassy and hence the catalyst can easily diffuse between them. The inter – particle diffusion of the catalyst is important for these reactions since only parts per million levels of catalyst are used in each experiment.

These results show that although using the standard reaction conditions it is not possible to make MMA macromonomers above a certain molecular weight, with the addition of the monomer shot a wider range of macromonomers may be prepared. The data from these experiments may be plotted on a *pseudo* Mayo type graph. Using the Mayo equation, if [CCTA] / [Monomer] is plotted versus $1/D_p$ of the final polymer then the gradient of the graph will be the chain transfer coefficient (Cs). Since many of the assumptions made in the Mayo equation are violated with these emulsion polymerisations it is only possible to plot a *pseudo*-Mayo plot (figure 2.10).

Figure 2.10 shows the effectiveness of the change in feed conditions for the experiment below 15 parts per million of catalyst. It can be seen that experiment M5 (100% fed) has a chain transfer much lower than for the other experiments, but for experiment M7 (20% shot of monomer / catalyst solution at the start of the reaction), the transfer constant is back up to the level for the experiments at higher catalyst concentrations.

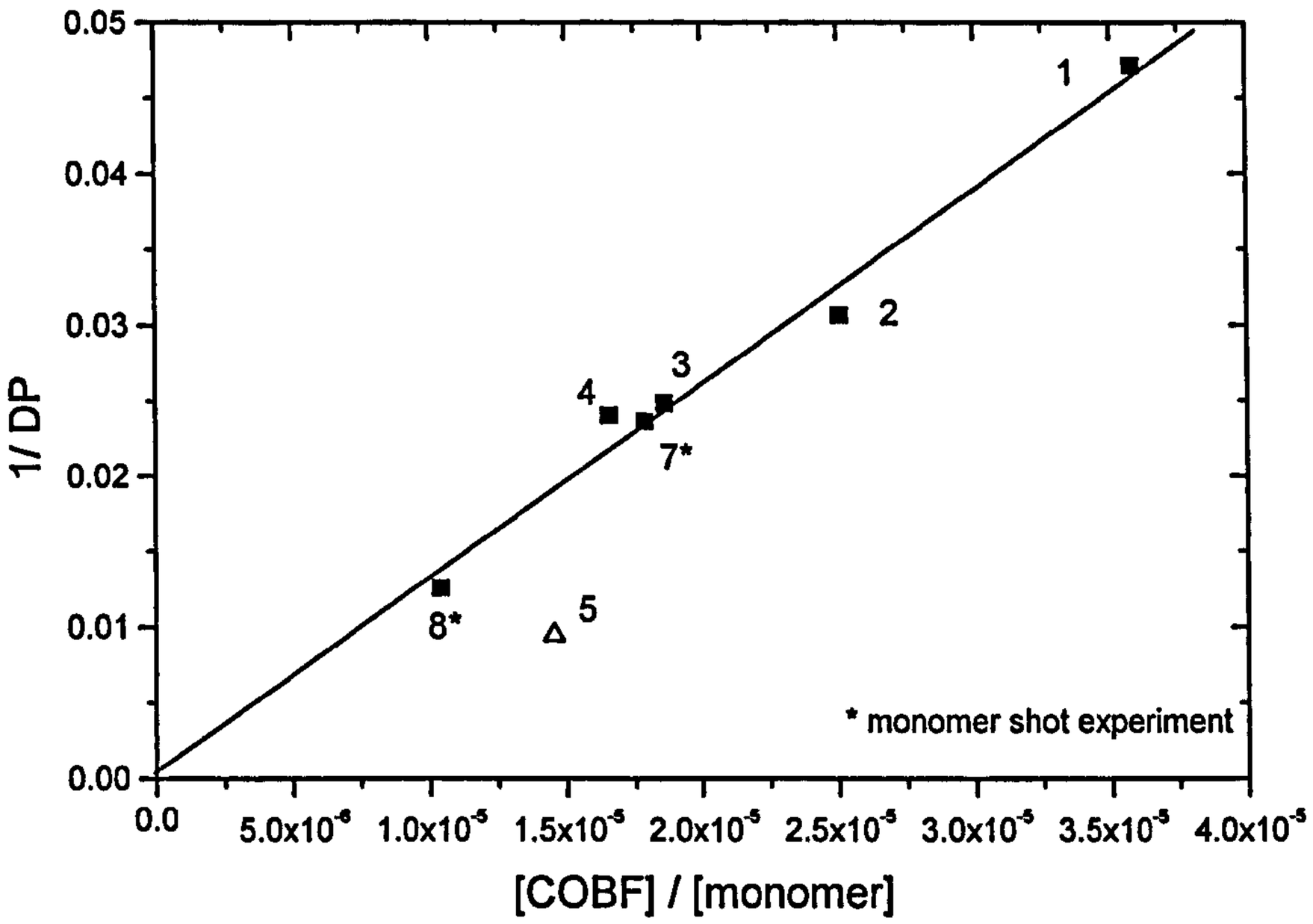

Figure 2.10 - *Pseudo Mayo plot for MMA emulsion polymerisations*

The Cs^E value given by the *pseudo* Mayo plot in figure 2.10 is 1300. This value does not take into account the level of partitioning of the catalyst between the water and monomer phases. If the partitioning is taken into account and the fact that there is more water than monomer present, then it is calculated that the Cs^E value would be closer to 6000.

2.3 The CCT Emulsion Polymerisation of a MMA/BMA Monomer Mixture.

It was postulated in the previous section that the change in transfer constant in the CCT emulsion polymerisation of MMA at low concentrations of COBF

(section 2.2) was due to the particles being glassy in nature at the reaction temperature. It was decided to polymerise a monomer set that would definitely have a T_g of under 80°C. A high molecular weight polymer of butyl methacrylate has a T_g of 20°C [7] and so an equimolar mixture of methyl methacrylate and butyl methacrylate was used to ensure a relatively low glass transition temperature.

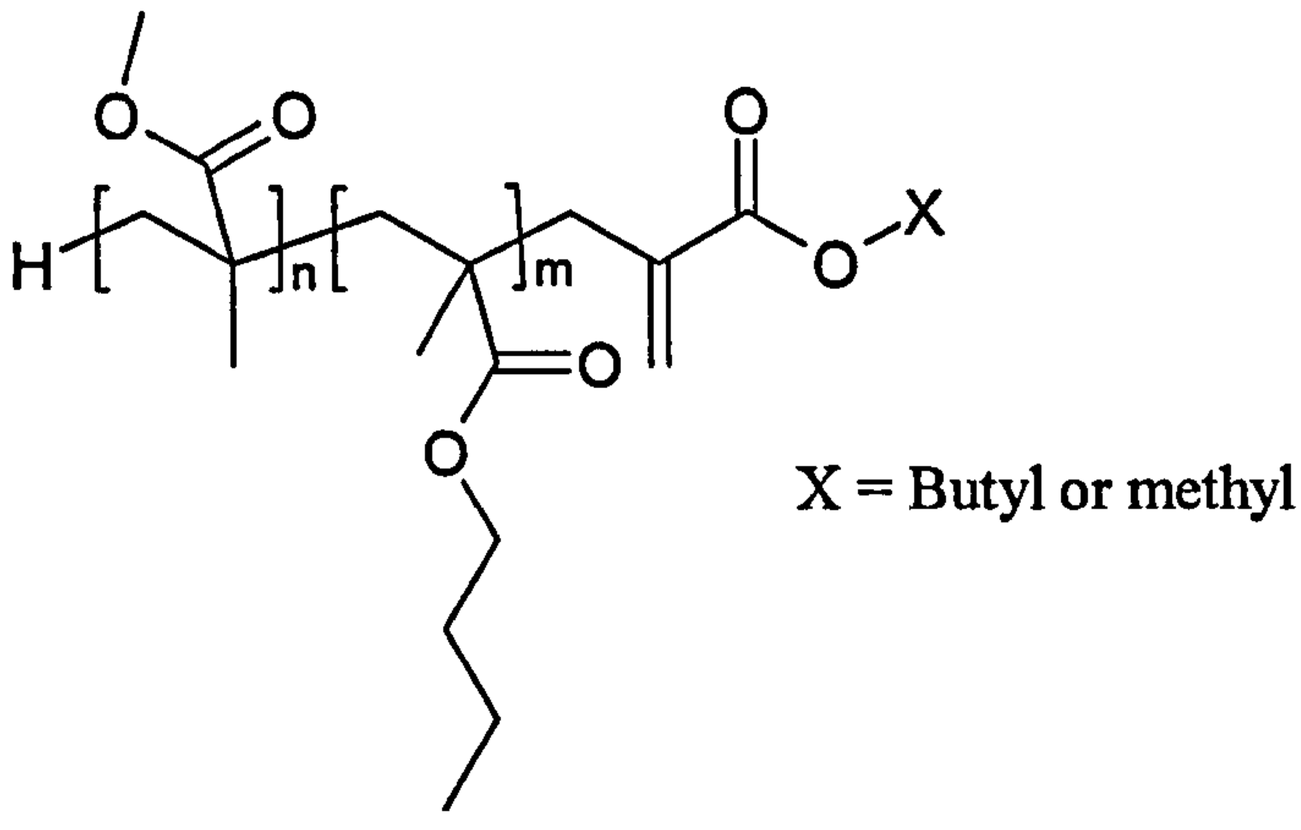

Figure 2.11 – *Structure of a statistical macromonomer made by CCT polymerisation of a mixture of MMA and BMA*

The structure shown in figure 2.11 is the one predicted for the CCT polymerisation of a mixture of BMA and MMA. The butyl and methyl methacrylate units will be distributed in a random or *statistical* manner.

Reaction	Wt. COBF (g)	Ppm COBF	Feed Conditions	Mn	PDi	Inst. Conv.	Cs^E
MB1	0.0243	36.04	100% fed	4880	2.35	0.981	689
MB2	0.0144	21.36	100% fed	7690	2.11	1.001	739
MB3	0.0076	11.27	100% fed	33400	1.95	1.020	323
MB4	0.0080	11.87	20% shot/ 80% fed	13300	2.24	0.965	766
MB5	0.0000	0.00	100% fed	93700	2.75	1.023	-

Table 2.4 – *End conditions for emulsion polymerisations MB1-MB6*

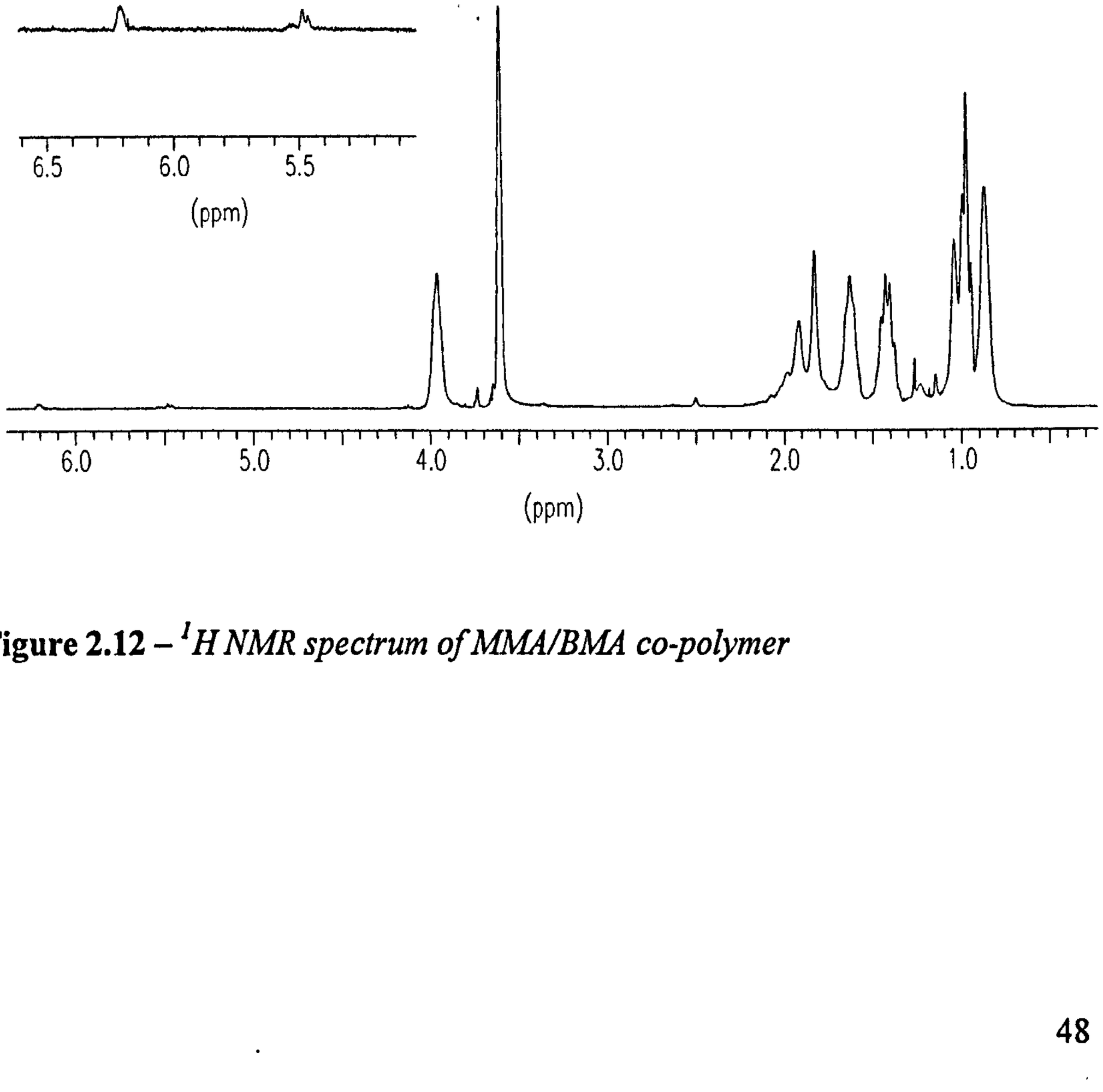

Figure 2.12 – *^1H NMR spectrum of MMA/BMA co-polymer*

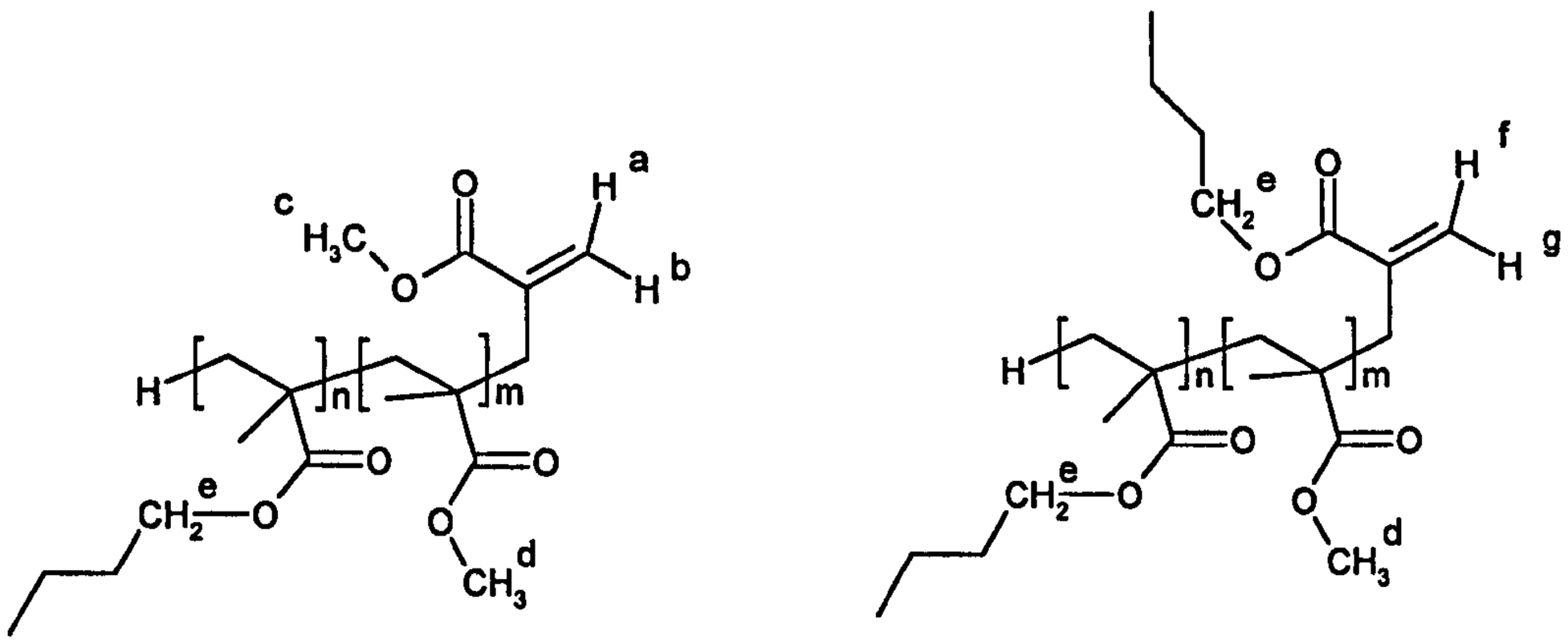

Figure 2.13 – *Structure of MMA/BMA polymers with protons labelled for NMR analysis*

Peak (ppm)	Integral	Multiplet Type	Assignment
6.21	1.00	(s)	Vinyl peak [a] or [f]
5.48 + 5.44	0.78	2 (s)	Vinyl peak [b] or [g]
3.96	53.19	(s)	Proton [e]
3.73	91.62	(s)	Terminal methoxy [c]
3.61		(s)	Methoxy in chain [d]
0.5 – 2.5	527.59	(m)	In chain CH_2 and CH_3 protons And remainder of butyl group

Table 2.5 – *NMR data for figure 2.12*

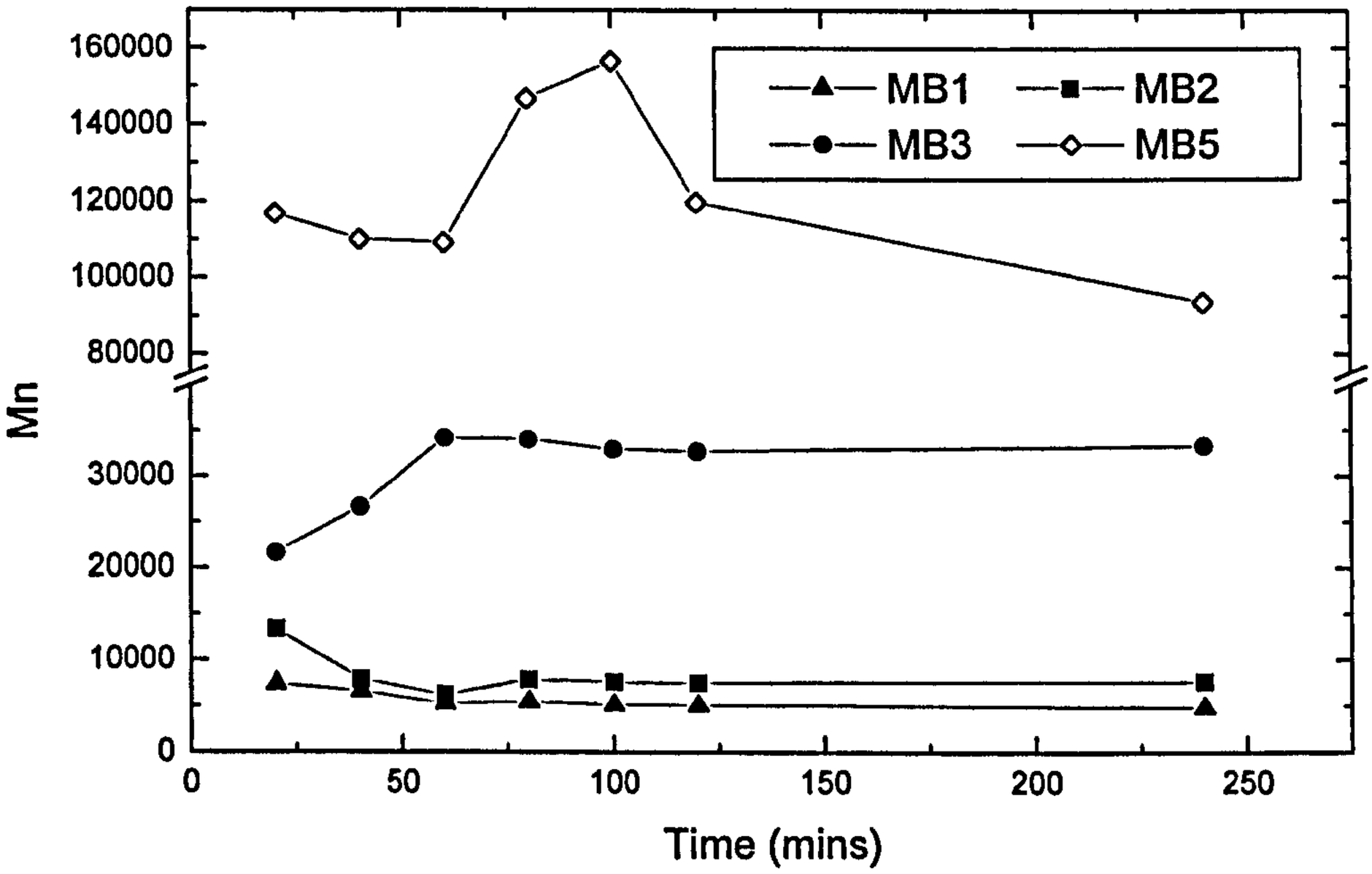

Figure 2.14 – *M_n versus time graph for polymerisations MB1, MB2, MB3 and MB5*

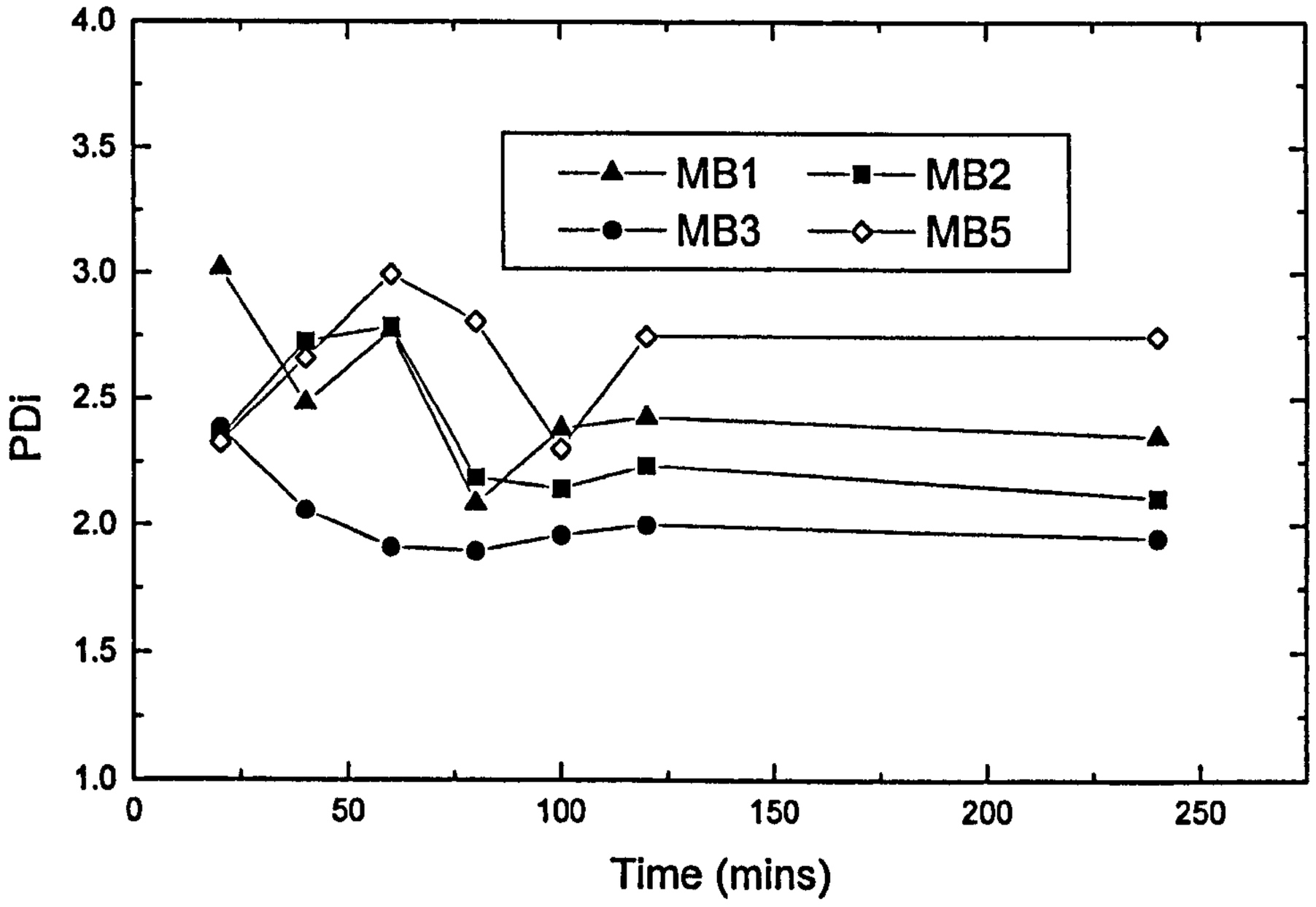

Figure 2.15 – *Polydispersity index versus time graph for polymerisations MB1, MB2, MB3 and MB5*

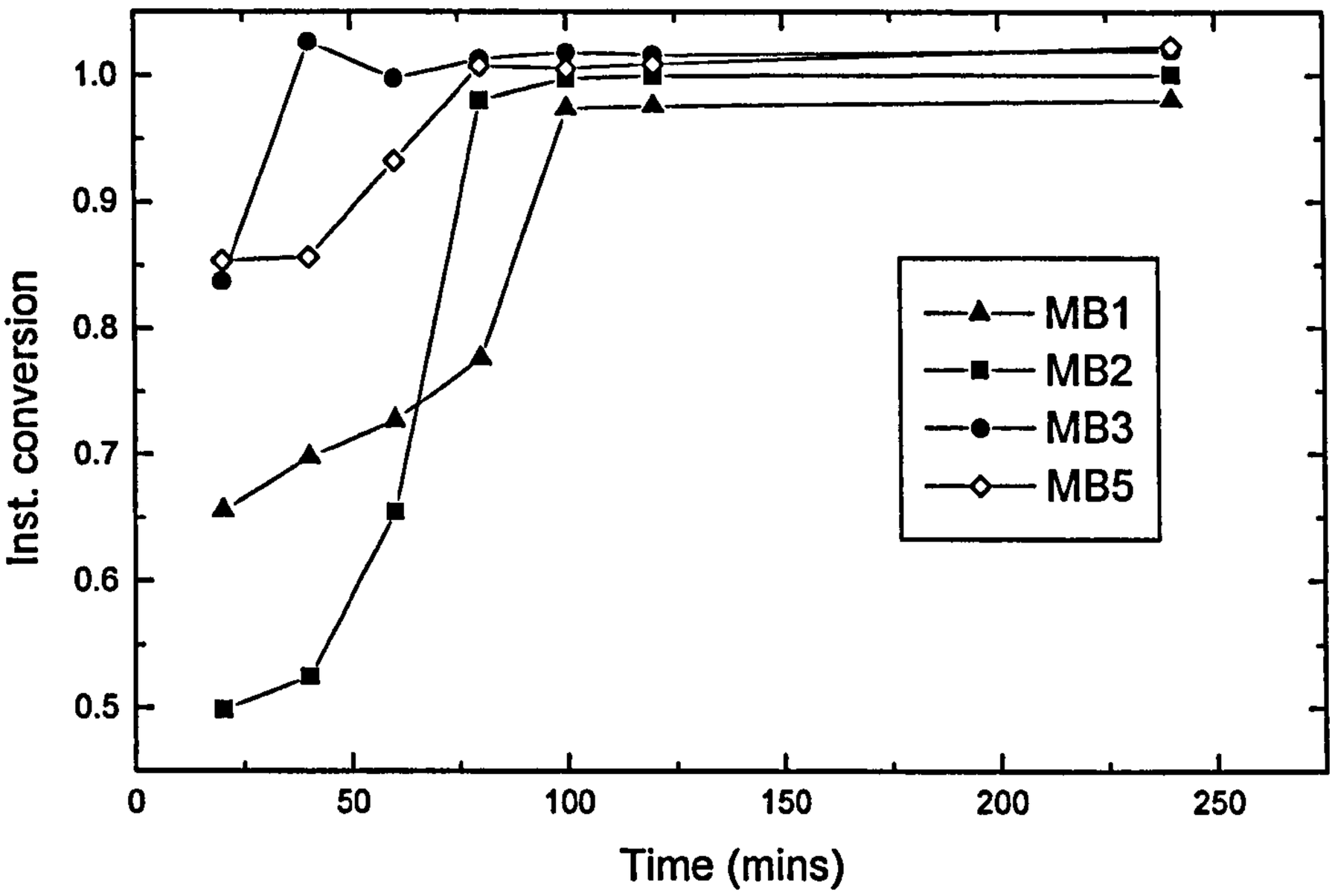

Figure 2.16 – *Instantaneous conversion versus time graph for polymerisations MB1, MB2, MB3 and MB5*

The results in table 2.4 and figures 2.14 and 2.15 show that as for the pure MMA emulsion polymerisations, COBF is effective in reducing the molecular weight of MMA/BMA co-polymers. The polydispersity index of the polymers formed is slightly higher than for the pure methyl methacrylate polymers but still close to the value of 2 which is acceptable for these types of reaction. It can be shown that for reaction MB3, which has a low level of catalyst, the CCT reaction did not operate efficiently. The molecular weight was higher than expected (indicating a lower Cs^E) and the rate of reaction, as shown by instantaneous conversion, was much faster than the reactions at higher catalyst concentrations. Analogously to the pure MMA case the reaction with the low amount of catalyst

operates under starved fed conditions and not under the non- starved fed reaction conditions necessary for efficient CCT in emulsion.

The predicted glass transition temperature of a BMA / MMA co-polymer with a 50:50 ratio of the monomers would be expected to be approximately 60 °C for high molecular weight polymer, (pure MMA has a Tg of 105 °C and BMA 20 °C[7]). The glass transition temperatures for the polymers synthesised in these experiments will be much lower than that predicted for high molecular weight polymers and hence under the reaction conditions (a polymerisation temperature of 80 °C) the particles should definitely not be glassy (see section 2.4 for the thermal analysis results). The change in activity of the catalyst cannot therefore be due to the transition between a glass and a rubber within the particles but must be due to the amount of monomer present in the particles. At early stages in the reaction the polymerisations at high catalyst concentrations will have relatively large amounts of monomer in the particles (at least 20 - 40% monomer) and this allows the free diffusion of catalyst around the system. In the case for the reactions with low catalyst concentration there is perhaps only 5 - 10% monomer present in the particles and the CCT agent will diffuse in and out of the particles much less readily. This is illustrated in figure 2.17.

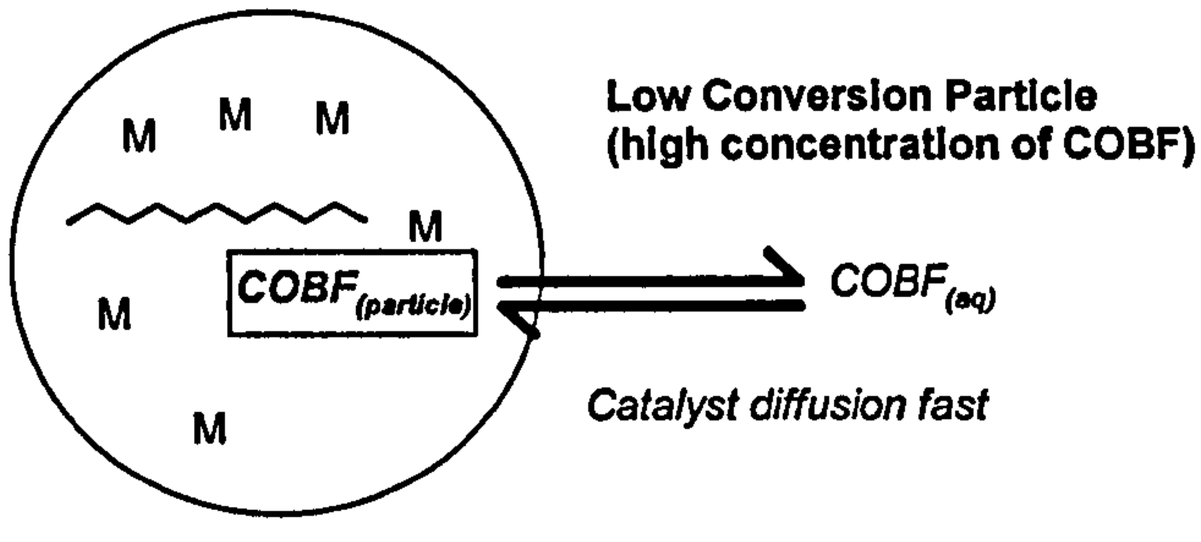

Figure 2.17 – *Illustration of catalyst movement in and out of polymer particles*

For experiment MB4 a shot of monomer and catalyst mixture was injected into the reactor immediately prior to the addition of the initiator and commencement of the monomer feed.

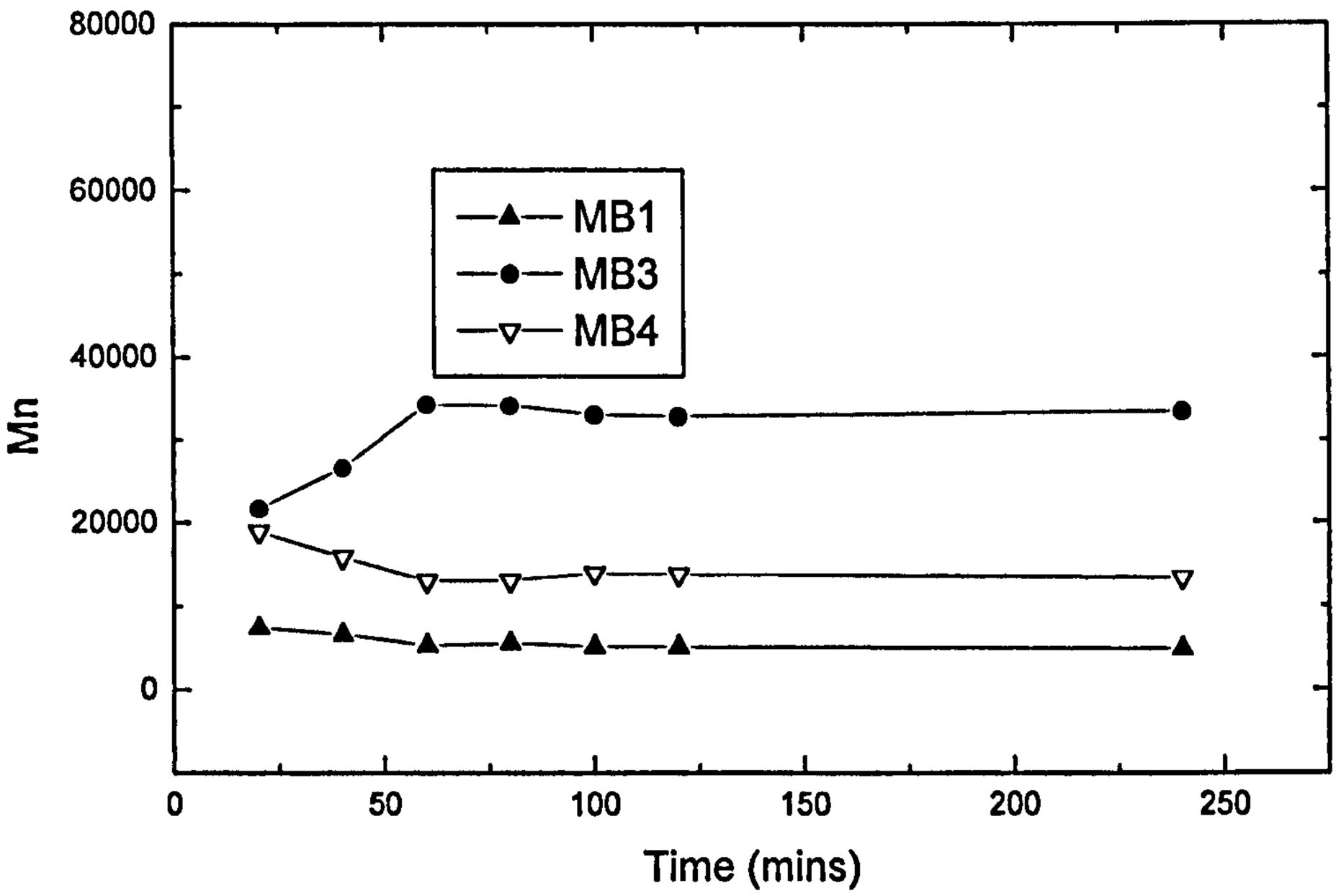

Figure 2.18 – *M_n versus time graph for polymerisations MB1, MB3 and MB4*

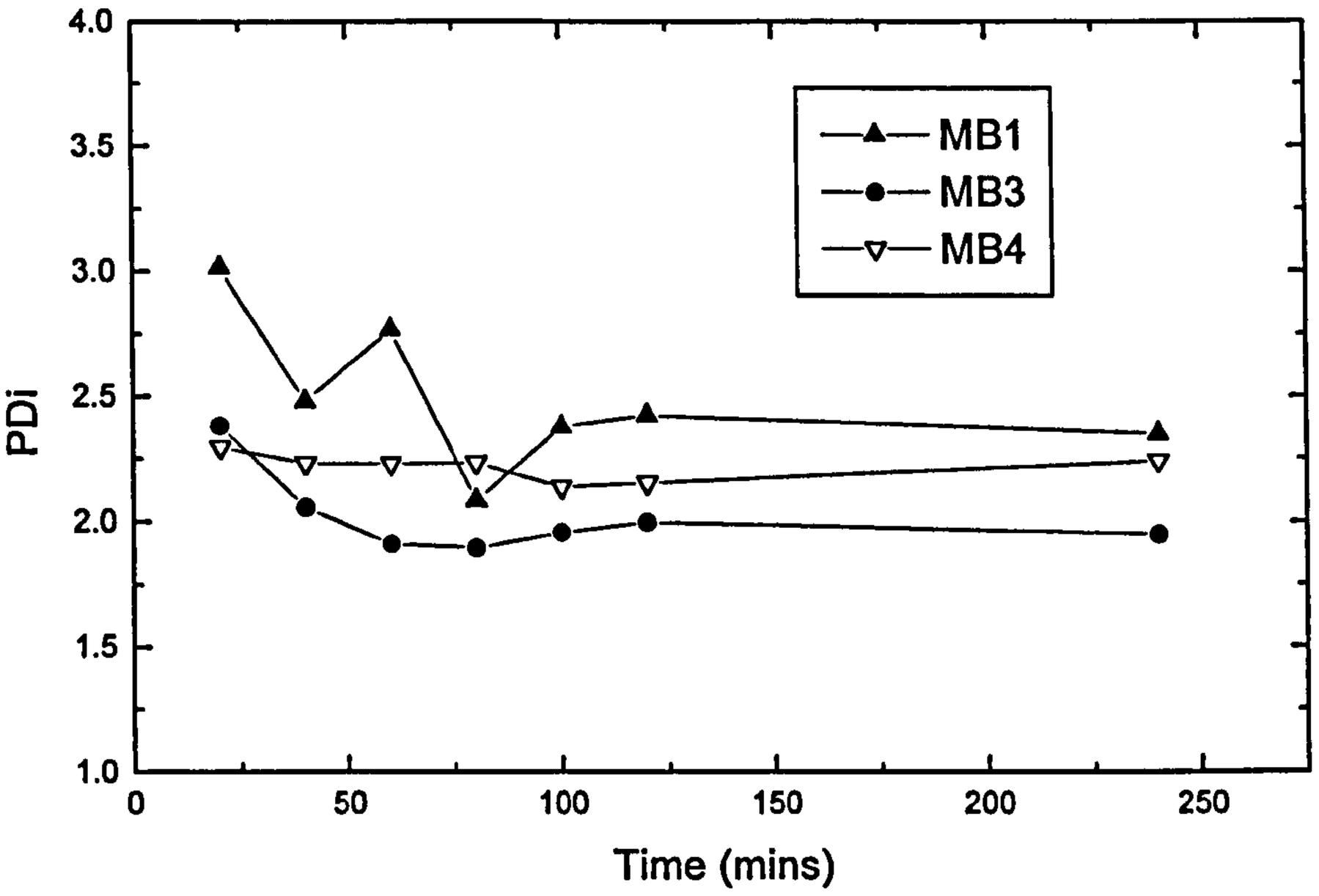

Figure 2.19 - Polydispersity versus time graph for polymerisations MB1, MB3 and MB4

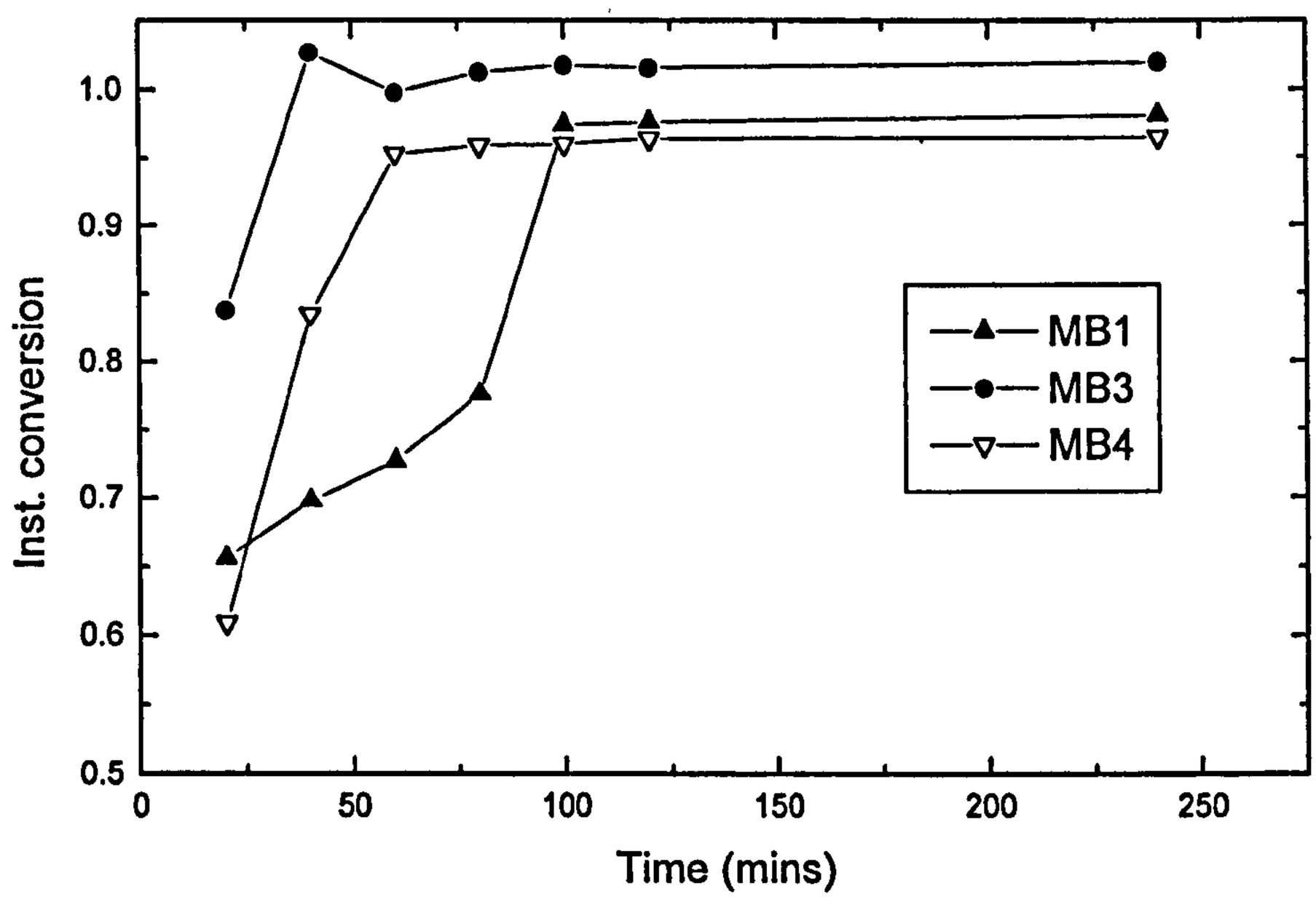

Figure 2.20 – *Instantaneous conversion versus time graph for polymerisations MB1, MB3 and MB4*

Figure 2.18 shows that the addition of the shot of monomer has increased the effective chain transfer constant (Cs^E value) for the reaction and lowered the molecular weight of the polymer produced. The instantaneous conversion versus time graph (figure 2.20) shows that for reaction MB4 the reaction has been slowed and been brought under starved fed conditions. Reaction MB4 is still much faster than for reaction MB1 due to the much lower amount of catalyst present in the reaction which slows the rate of polymerisation.

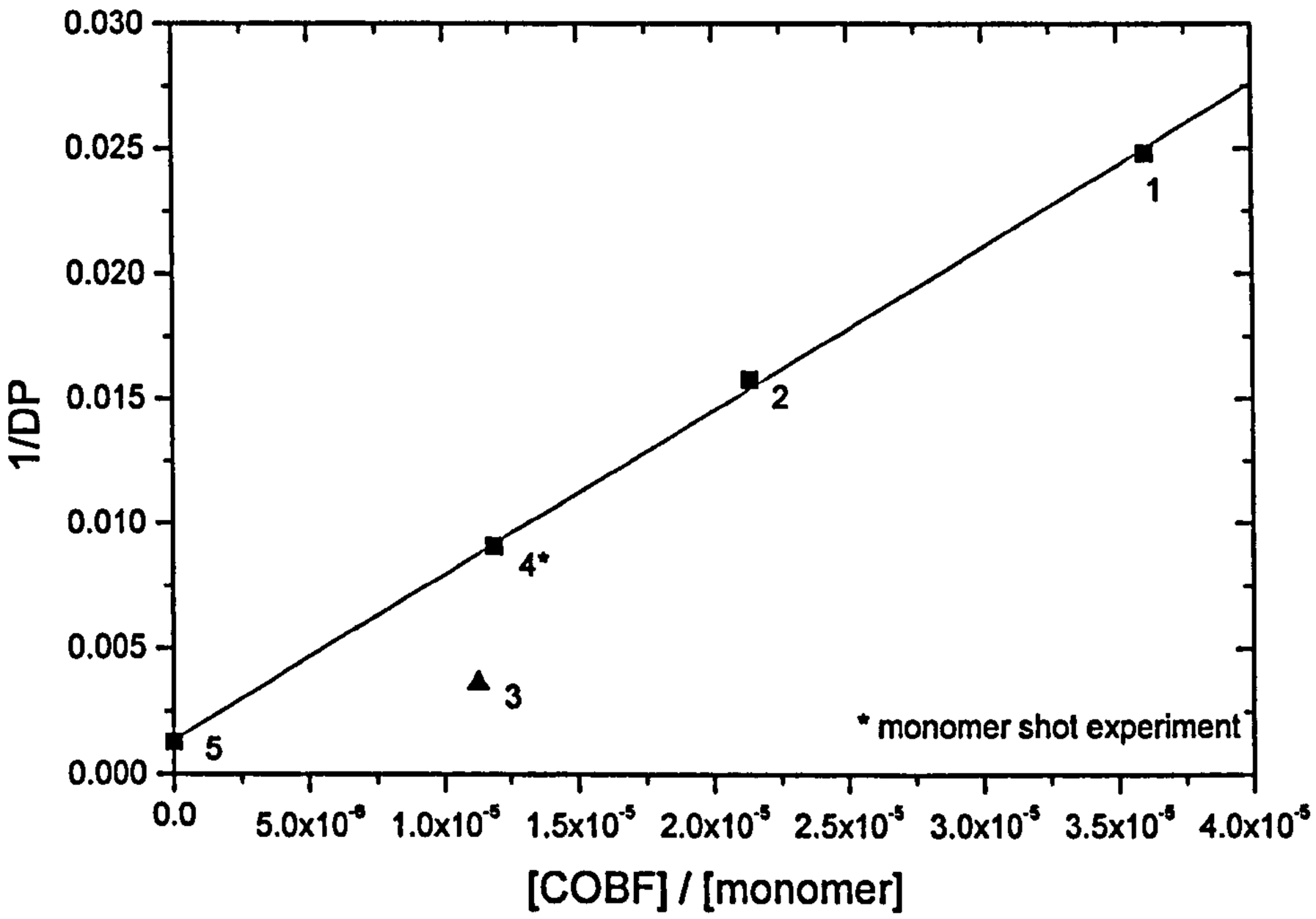

Figure 2.21 - *Pseudo Mayo plot for MMA/BMA co-polymerisations*

Figure 2.21 shows a *pseudo* Mayo plot for CCT reactions in emulsion for MMA/BMA co-polymers (50:50 molar ratio). The shot of monomer for reaction MB4 has brought the effective chain transfer constant up to the level of the reactions with higher concentrations of catalyst. The average chain transfer

constant for these reactions given by the gradient for these graphs is 730. The Cs^E value is lower than that for the equivalent pure MMA reaction. It has been shown that for bulk CCT reactions that COBF has a lower chain transfer constant for BMA than for MMA[8] partly due to the higher k_p of BMA (since $C_s = k_{tr}/k_p$) As described in section 1.7 it has been postulated that the CCT reaction is diffusion controlled and the increase in viscosity of the larger monomers decreases the diffusion coefficients in the system which could have the effect of lowering the transfer constant.

The reduced observed catalytic activity is also partly due to the fact that butyl methacrylate is more hydrophobic than methyl methacrylate and so the catalyst will partition more into the water phase effectively lowering the concentration of COBF at the locus of polymerisation (the particles).

2.4 The CCT Emulsion Polymerisation of BMA

It was found in the previous section that using a MMA/BMA mixture to ensure a glass transition temperature below that of the reaction temperature did not have the desired effect on the reaction, i.e. a threshold catalyst concentration was still observed. In this section the glass transition temperature was depressed even lower to observe what effect this would have. Pure BMA macromonomers were synthesised by CCT emulsion polymerisation to see if the very low glass transition temperature would allow more effective movement of the catalyst between high conversion paricles. The predicted structure for the polymer synthesised by CCT of butyl methacrylate is shown in figure 2.22.

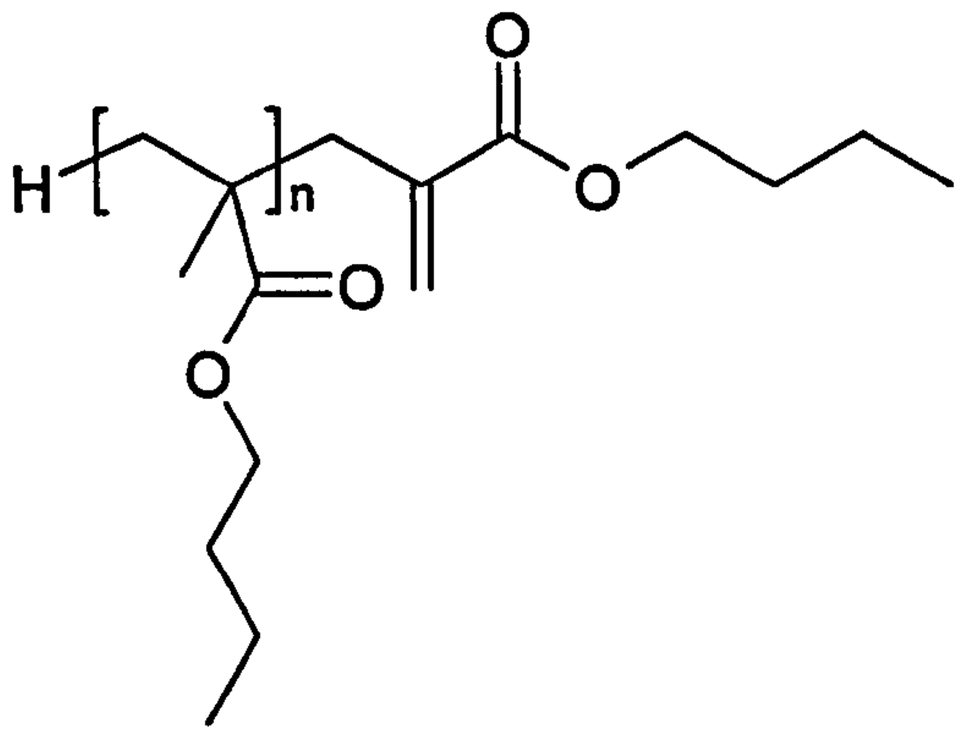

Figure 2.22 – *Structure of BMA macromonomer*

The results for the BMA emulsion polymerisations are shown in table 2.6.

Reaction	Wt. COBF (g)	Ppm COBF	Feed Conditions	Mn	PDi	Inst. Conv.	Cs^E
B1	0.0163	28.88	100% fed	7820	3.62	0.971	630
B2	0.0119	21.09	100% fed	11300	3.40	0.998	595
B3	0.0062	10.99	100% fed	64400	2.52	1.009	201
B4	0.0060	10.63	20% shot 80% fed	45200	2.31	0.980	296
B5	0.0000	0.00	100% fed	191000	2.18	0.939	-

Table 2.6 – *End conditions for polymerisations B1-B5*

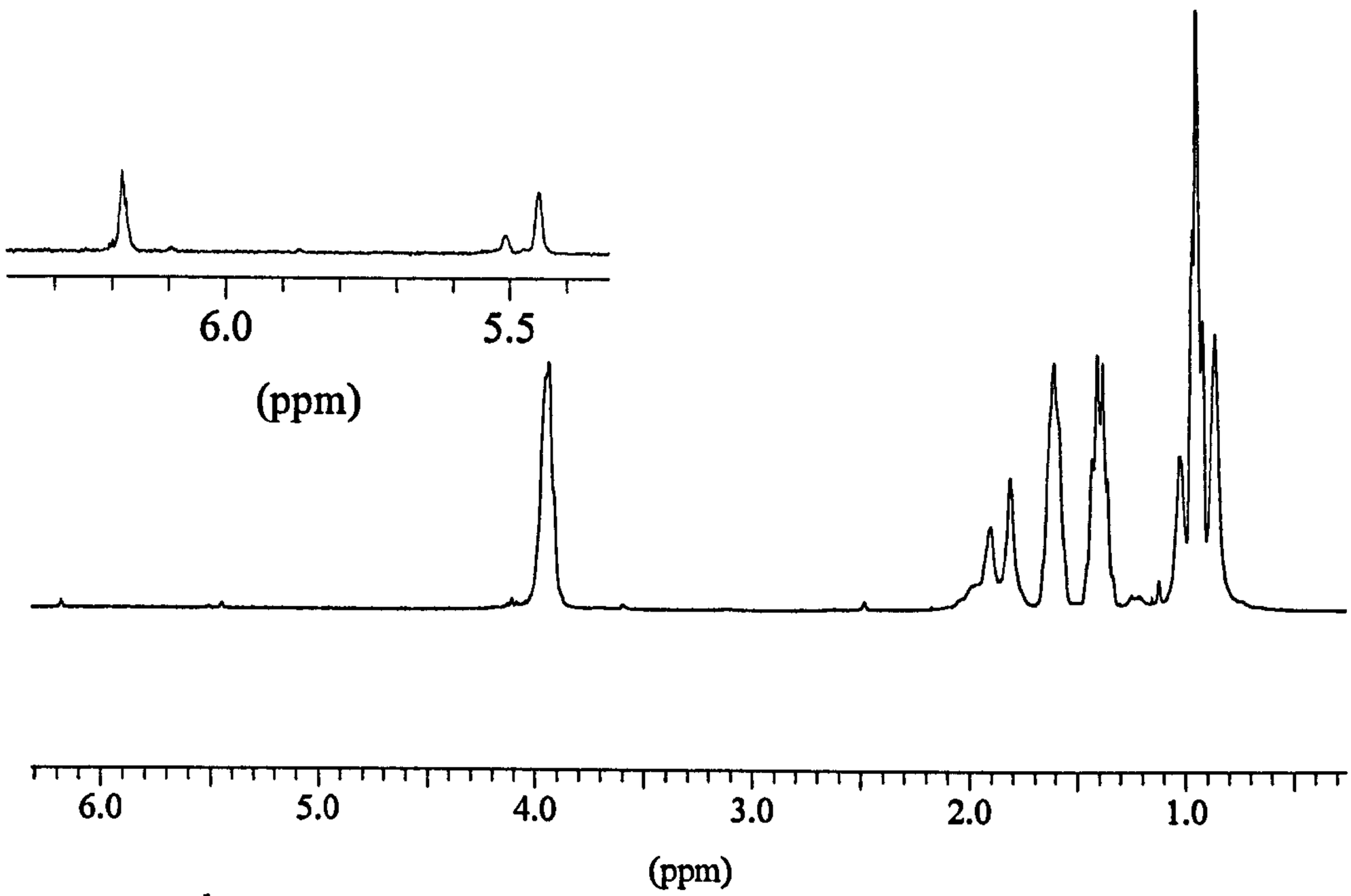

Figure 2.23 – *^{1}H NMR spectrum of BMA macromonomer*

Peak (ppm)	Integral	Multiplet Type	Assignment
6.18	1.00	(s)	Vinyl peak [a]
5.51 + 5.45	1.01	(s)	Vinyl peak [b]
3.93	146.15	(s)	Butoxy CH_2 [c]
0.5 – 2.5	155.90	(m)	In chain CH_2 and CH_3 protons And remainder of butyl group

Table 2.7 – *NMR data for the spectrum shown in figure 2-21*

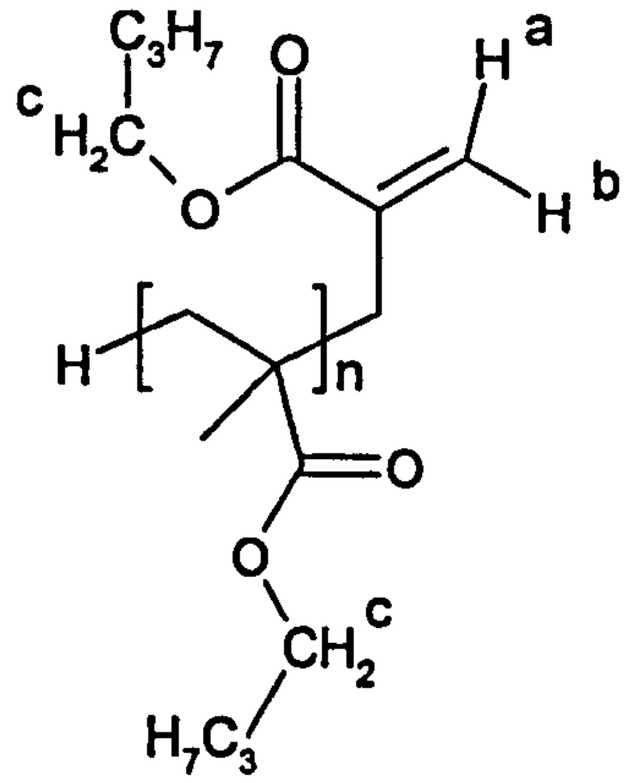

Figure 2.24 – *Structure of PBMA with protons labelled for NMR analysis*

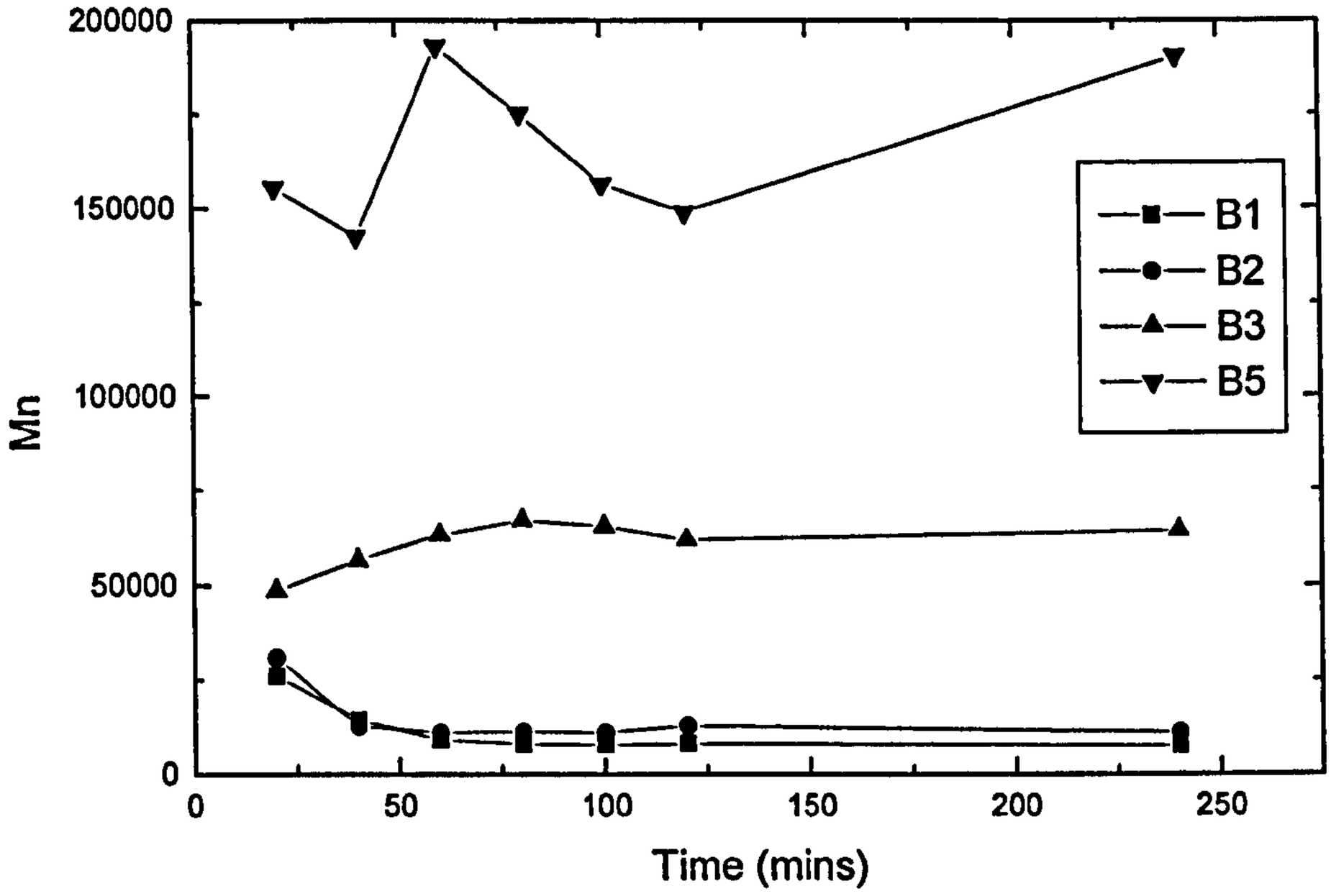

Figure 2.25 – *M_n versus time graph for polymerisations B1-B3 and B5*

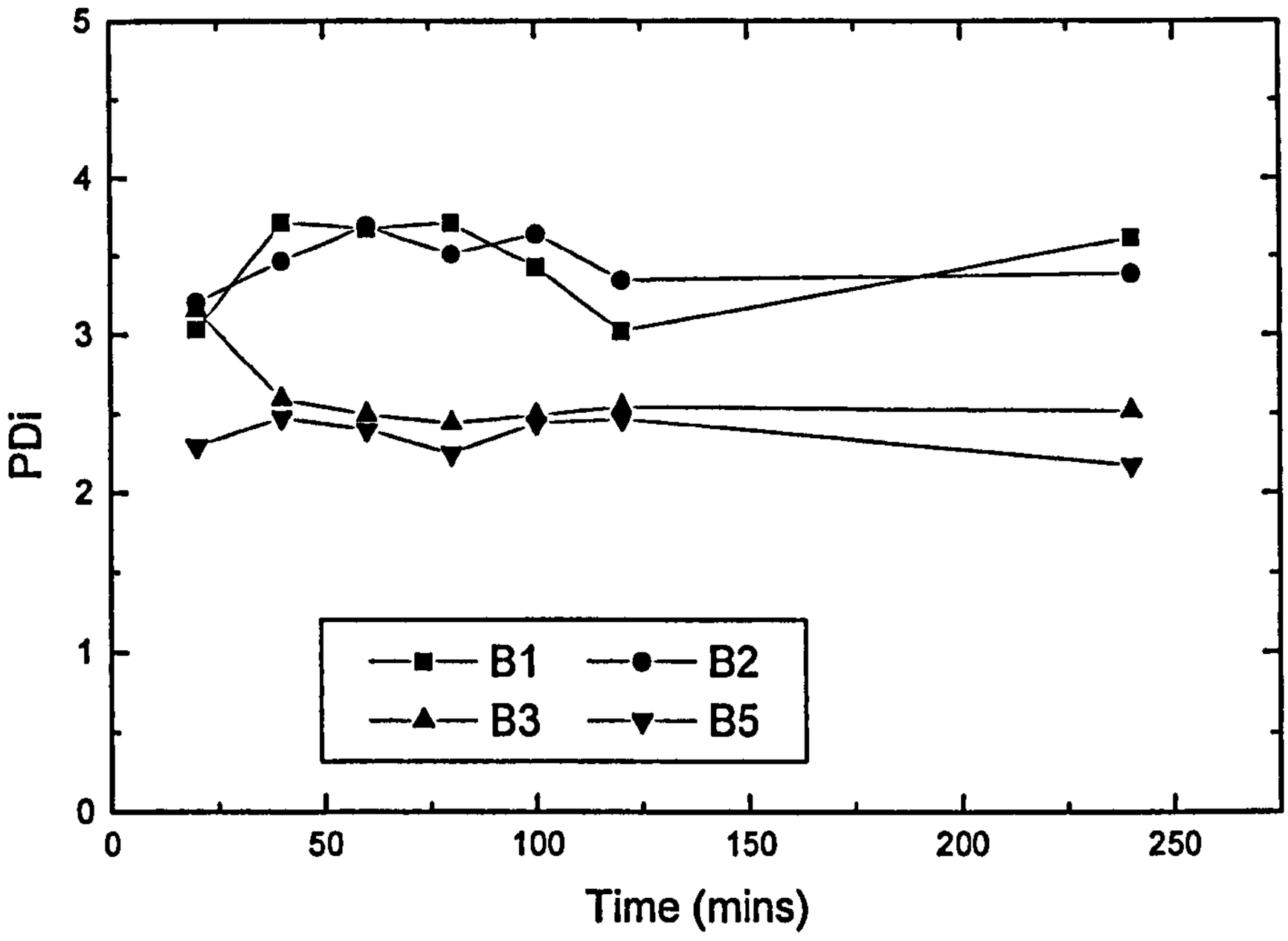

Figure 2.26 – *Polydispersity index versus time graph for polymerisations B1-B3 and B5*

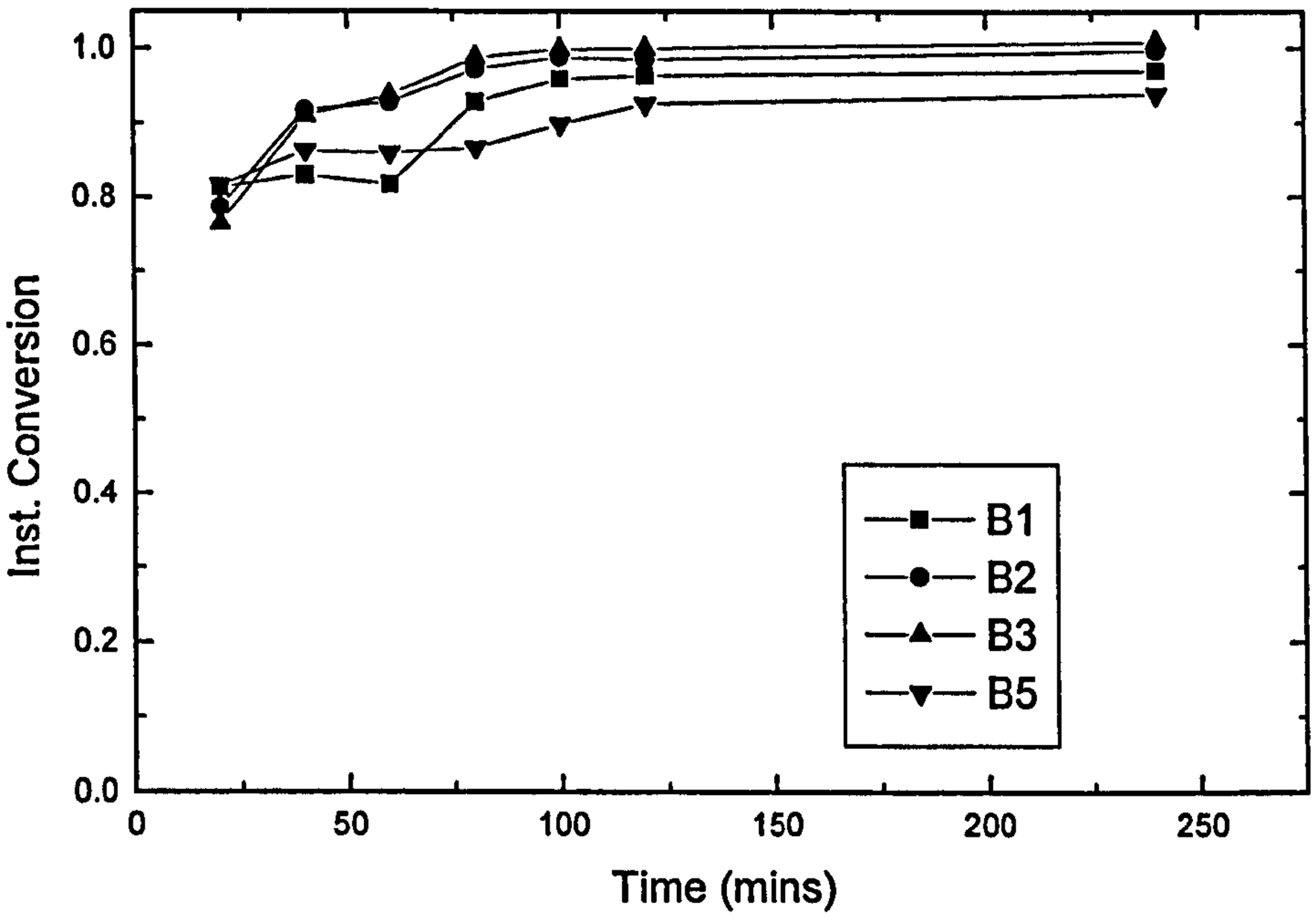

Figure 2.27 – *Instantaneous conversion versus time graph for polymerisations B1-B3 and B5*

The molecular weight data for the CCT reactions for pure BMA polymerisations show similar results to those observed for pure MMA and for MMA/BMA co-polymers. On the addition of COBF catalyst the molecular weight is reduced compared to the control reaction (MB5, 0 ppm COBF). The rate of reaction is high in all of the polymerisations and there is little difference between the control reaction and the ones with catalyst present. All of the CCT reactions appear to be under starved fed conditions which it was previously postulated would not give efficient chain transfer in emulsion, however, the CCT reaction does appear to be effective under these conditions. An explanation of this may be due to the very low glass transition temperature of BMA which could mean that less monomer is necessary in the particles to allow free transport of the catalyst.

Again it is observed that at low catalyst concentrations (reaction B3) there is a reduction in catalyst activity. As reactions B1 and B2 are carried out under starved fed conditions it is not expected that an addition of a shot of monomer to reaction B3 would have the same effect as in the MMA and MMA/BMA cases and indeed what is observed supports this hypothesis (figures 2.28- 2.30).

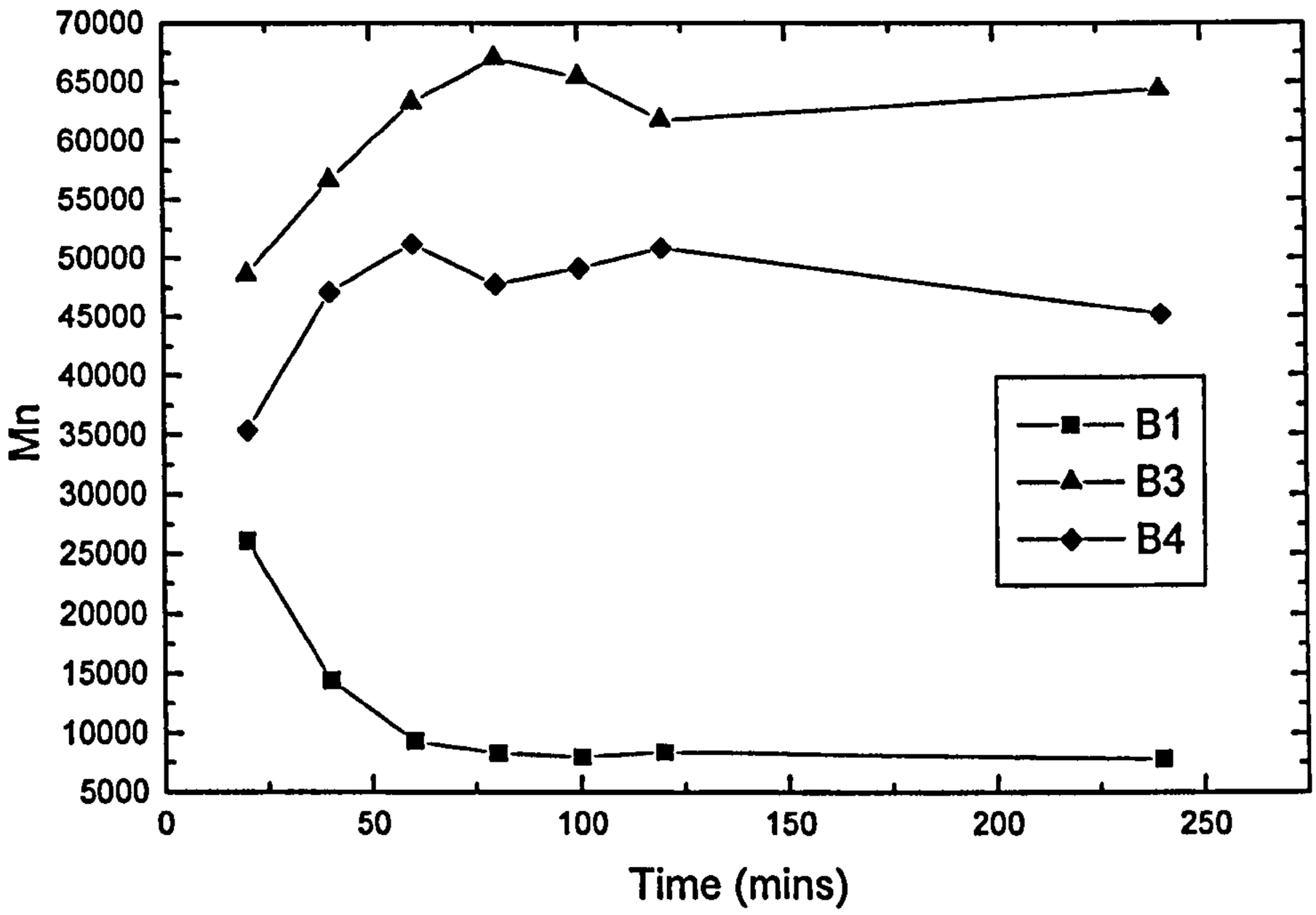

Figure 2.28 - *M_n versus time graph for polymerisations B1, B3 and B4*

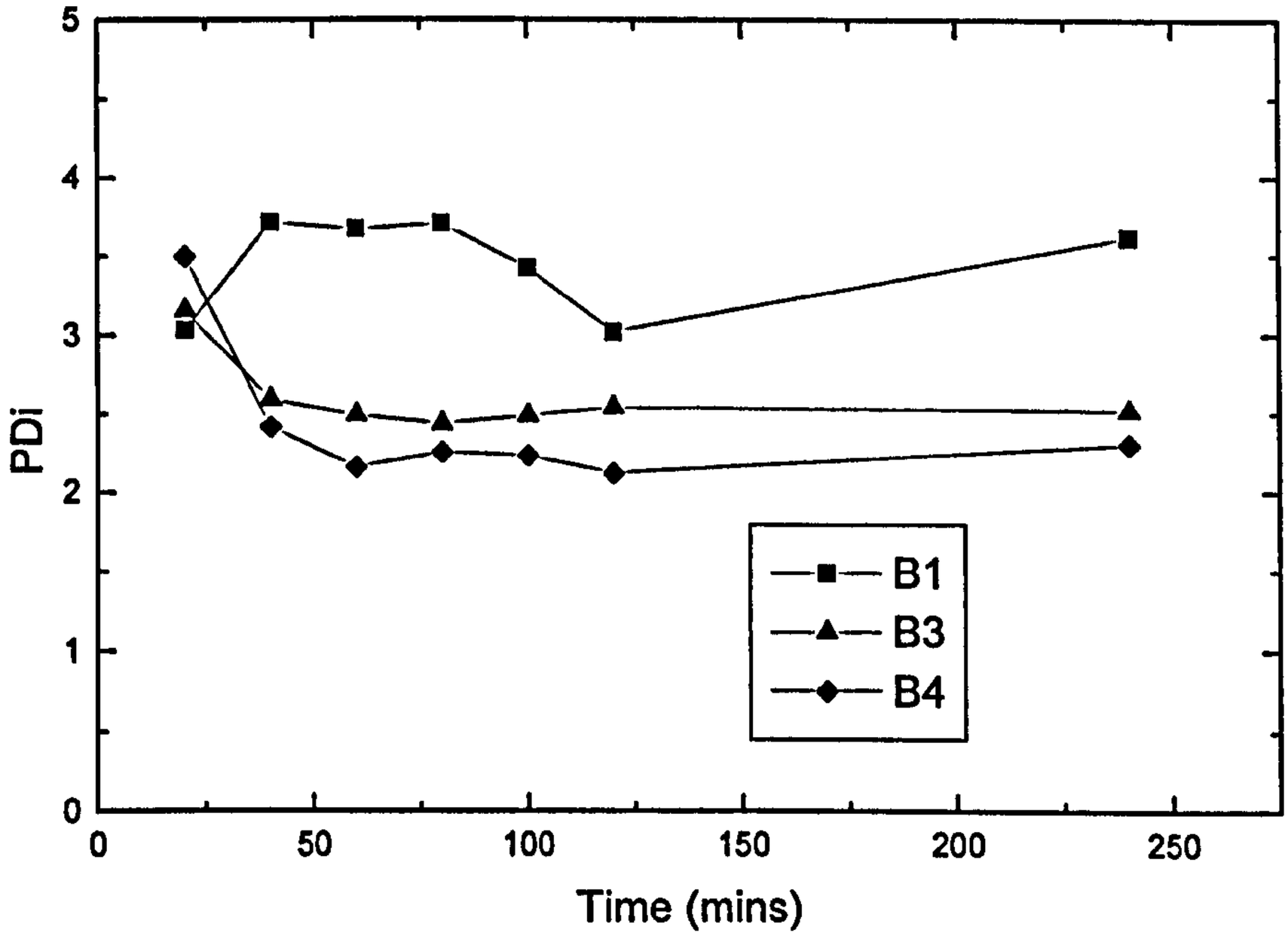

Figure 2.29 - *Polydispersity versus time graph for polymerisations B1, B3 and B4*

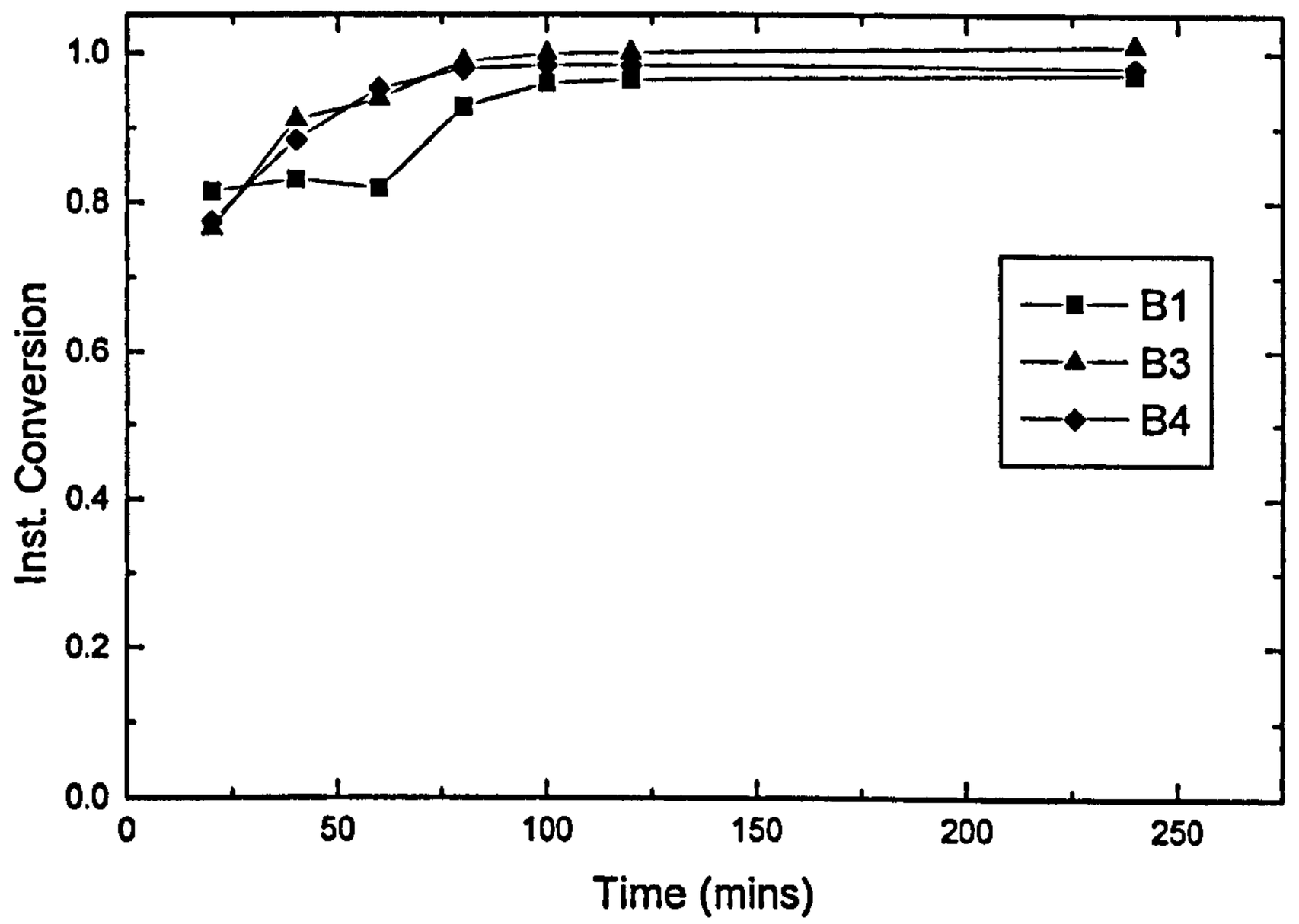

Figure 2.30 – *Instantaneous conversion versus time graph for polymerisations B1, B3 and B4*

Figures 2.28-2.30 show that the addition of the monomer shot had little effect on the reaction. The molecular weight of the polymer produced in reaction B4 has not been significantly reduced compared to reaction B3, showing that the transfer activity has been only slightly increased on the addition of the monomer shot.

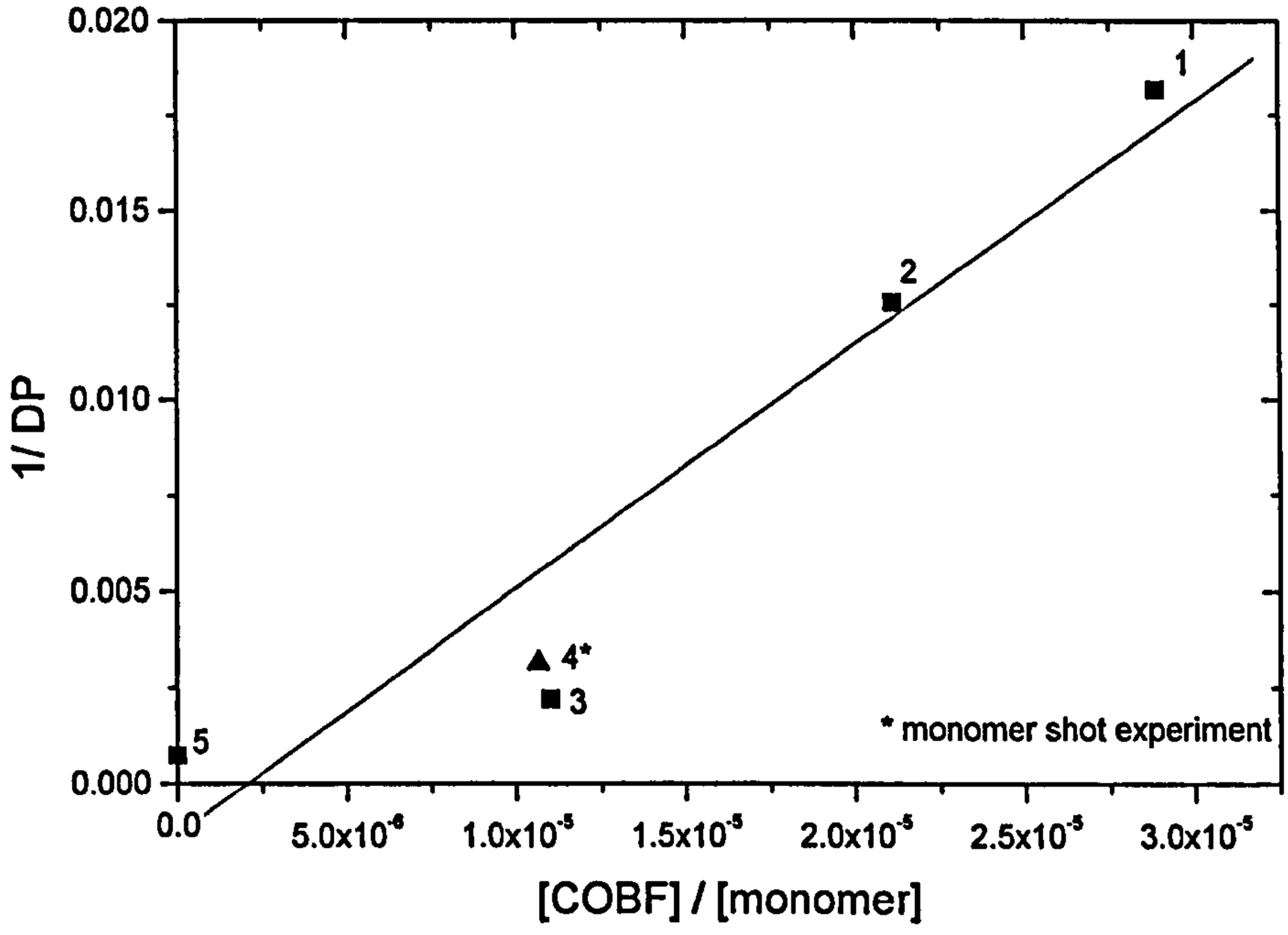

Figure 2.31 – *Pseudo Mayo plot for BMA emulsion polymerisations*

The *pseudo* mayo plot for reactions B1-B5 gives a Cs^E value of 600 which is lower than for the pure MMA and BMA/MMA co-polymers. Again the increased hydrophobic nature of the monomer affecting the catalyst partitioning and the natural tendency of COBF to have a lower Cs value with BMA result in a lower observed transfer constant.

2.4 Thermal Analysis

The thermal analysis of a synthesised polymer is often of great importance since the application of a particular polymer may depend on its thermal behaviour. The glass transition temperature (T_g) of a polymer is the point at which it goes from a glass to a rubber. For a polymer used for its mechanical strength the T_g would be required to be well above the working temperature of the polymer. Alternatively if a rubbery material is required the T_g would need to be well below normal working temperatures.

2.4.1 Differential Scanning Calorimetry (DSC) of MMA, MMA-*co*-BMA and BMA Polymers Made by CCT Emulsion Polymerisation

It has been shown that the glass transition temperature of poly(methyl methacrylate) is molecular weight dependent at low molecular weights and that at higher molecular weights the glass transition temperature reaches a limiting value[9-11]. The glass transition temperature of methacrylate polymers synthesised by CCT polymerisation in emulsion were measured using differential scanning calorimetry. The results for the PMMA polymers are shown below in table 2.8.

Reaction	M_n	M_w	Tg (°C) Onset	Tg (°C) inflection
M1	2120	3500	64	77
M2	3260	5770	78	90
M3	4030	7700	90	99
M4	4160	7900	92	98
M5	10500	41200	106	114
M6	4230	7570	93	99
M7	7940	14300	107	111

Table 2.8 – *DSC results of MMA polymers*

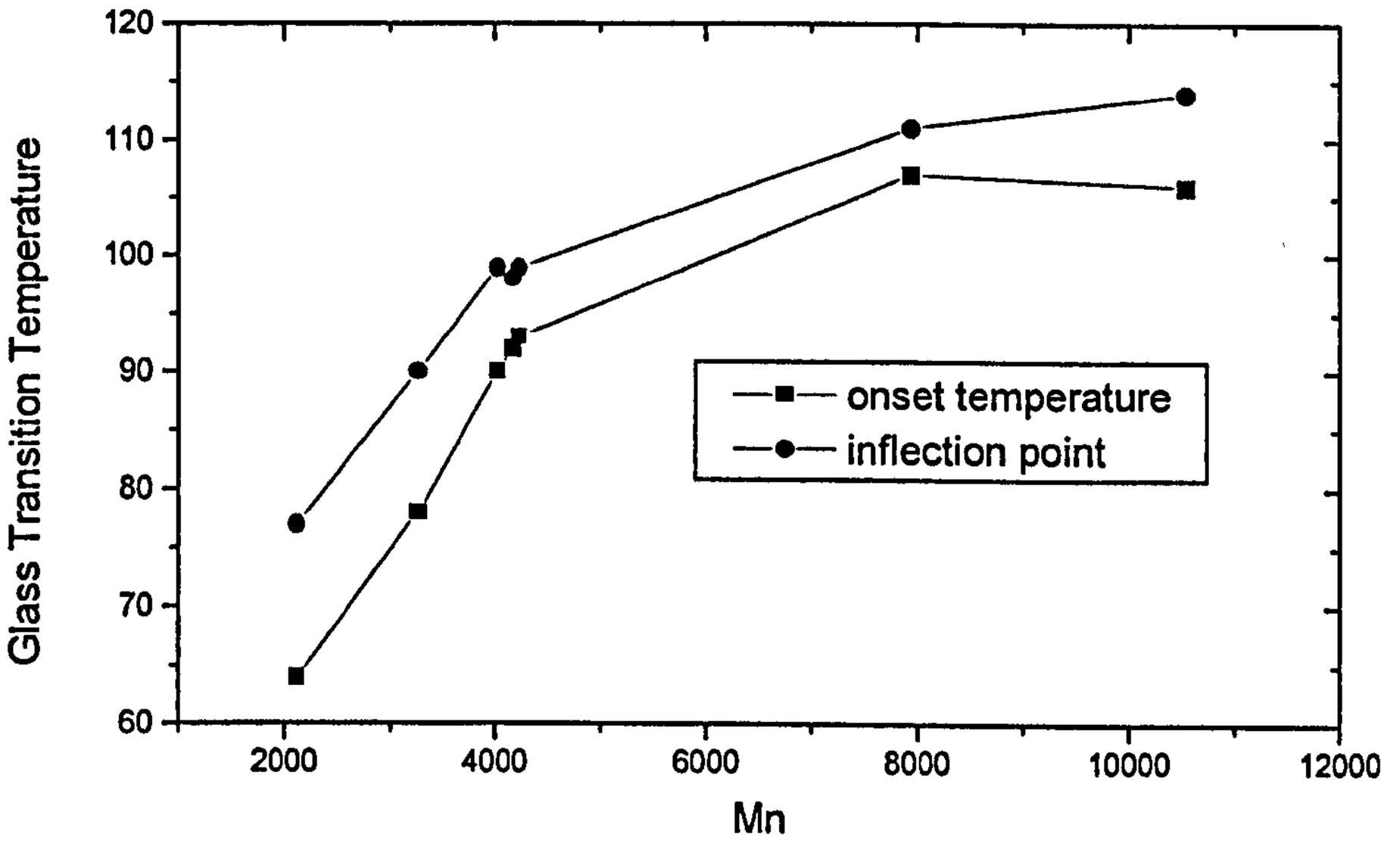

Figure 2.32 – *Glass transition temperature versus M_n graph for MMA polymers*

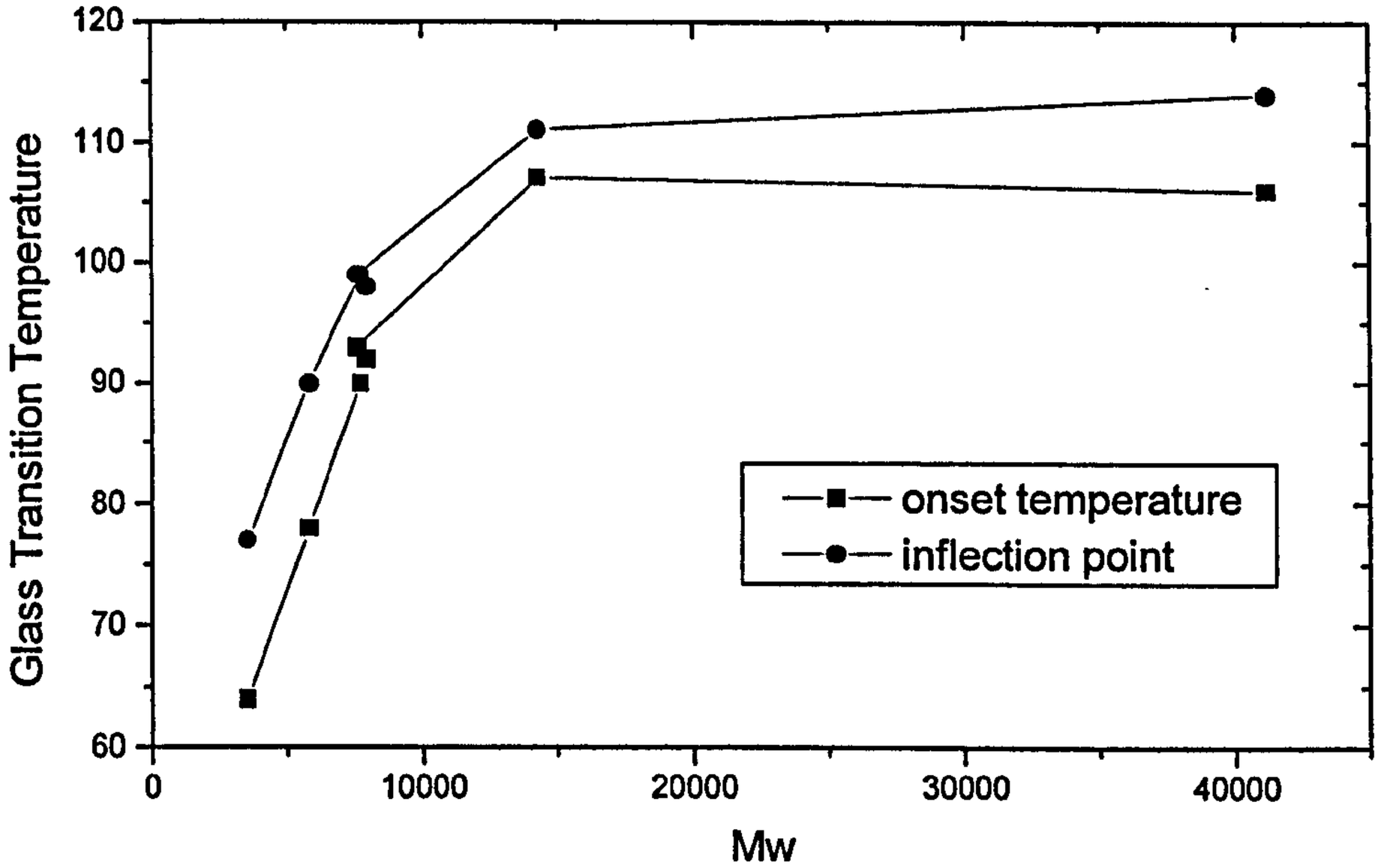

Figure 2.33 – *Glass transition temperature versus Mw graph for MMA polymers*

Figures 2.32 and 2.33 show clearly the increase in glass transition temperature as a function of molecular weight. Below an M_w of 10,000 the T_g of the formed polymer rises rapidly with increasing molecular weight and shows that using the CCT reaction the glass transition temperature of a methacrylate polymer can be accurately tuned to the desired value as opposed to the usual method of adding a co-monomer. Above the M_w value of approximately 10,000 the glass transition temperature is much less sensitive to changes in molecular weight. These results are very consistent with those shown by O'Driscoll et al[11]. The Flory and Fox description of the chain length dependence[10] of glass transition temperature states that :

$$T_g = T_{g\infty} - K / Dp \qquad (2.1).$$

$T_{g\infty}$ is the limiting glass transition temperature at high molecular weight and K is a constant. It can be seen that the glass transition temperature will rapidly reach a value where increasing the molecular weight will not have much effect on the glass transition temperature of the polymer. A linear least squares analysis was performed on the data in table 2.8 to yield the predicted curve shown in figure 2.34.

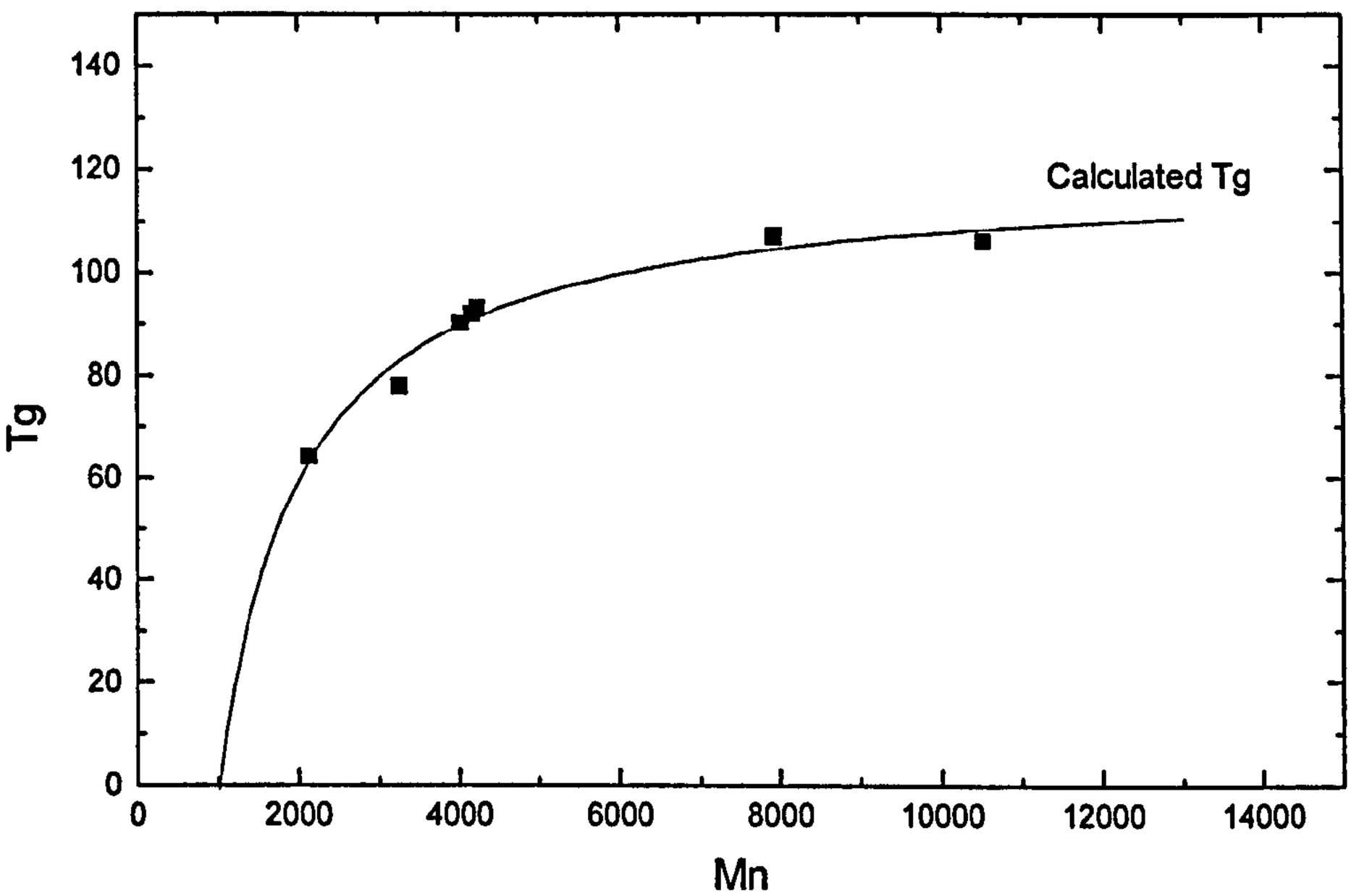

Figure 2.34 – *Predicted glass transition temperature (onset temperature) and experimental values versus M_n graph for MMA polymers*

With the linear least squares analysis of the data shown in table 2.8 it is found that a limiting $T_{g,\infty}$ of 392 K (119 °C) and a K constant value of 1205 best fitted the data. The data was also fitted using M_w rather than M_n data but it was found that the data fitted using the M_n data had less error associated with it.

Reaction	M_n	M_w	Tg (°C) Onset	Tg (°C) inflection
MB1	4880	11500	21	33
MB2	7690	16200	46	56
MB3	33400	65000	55	67
MB4	13300	29900	52	63
MB5	93700	258000	60	75

Table 2.8 – *DSC results for MMA/BMA co-polymers*

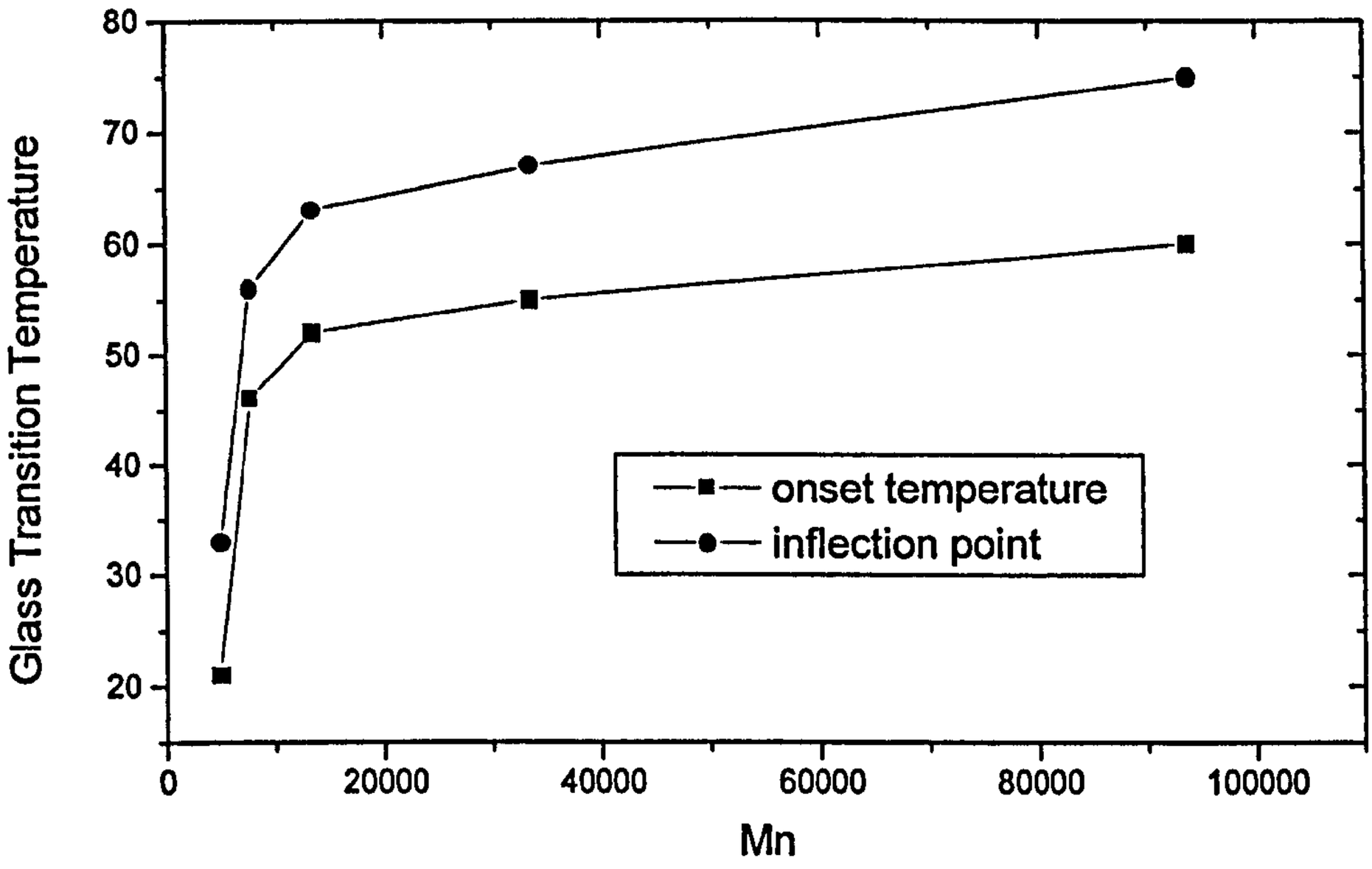

Figure 2.35 – *Glass transition temperature versus M_n graph of MMA/BMA co-polymers*

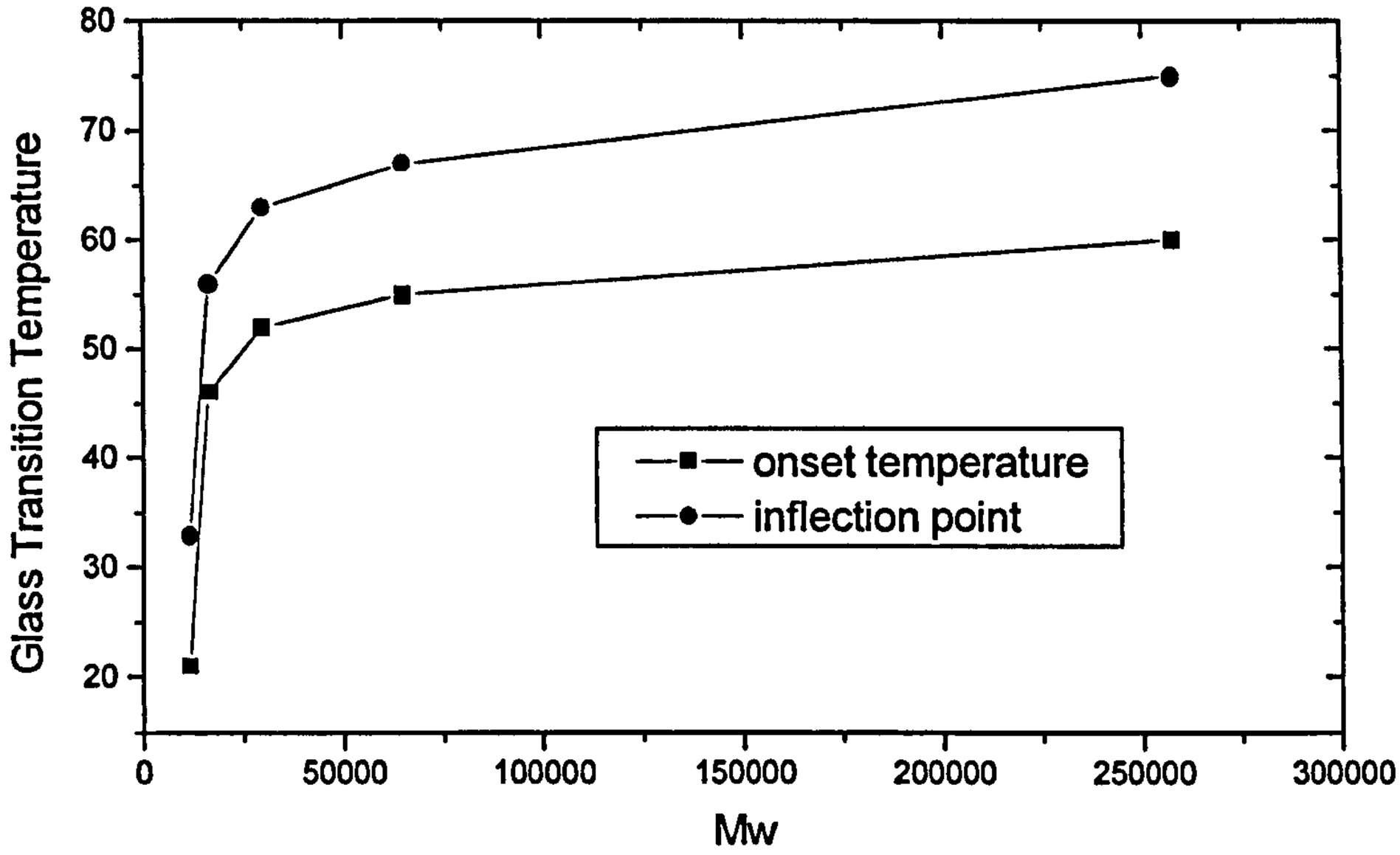

Figure 2-36 – *Glass transition temperature versus M_w graph for MMA/BMA co-polymers*

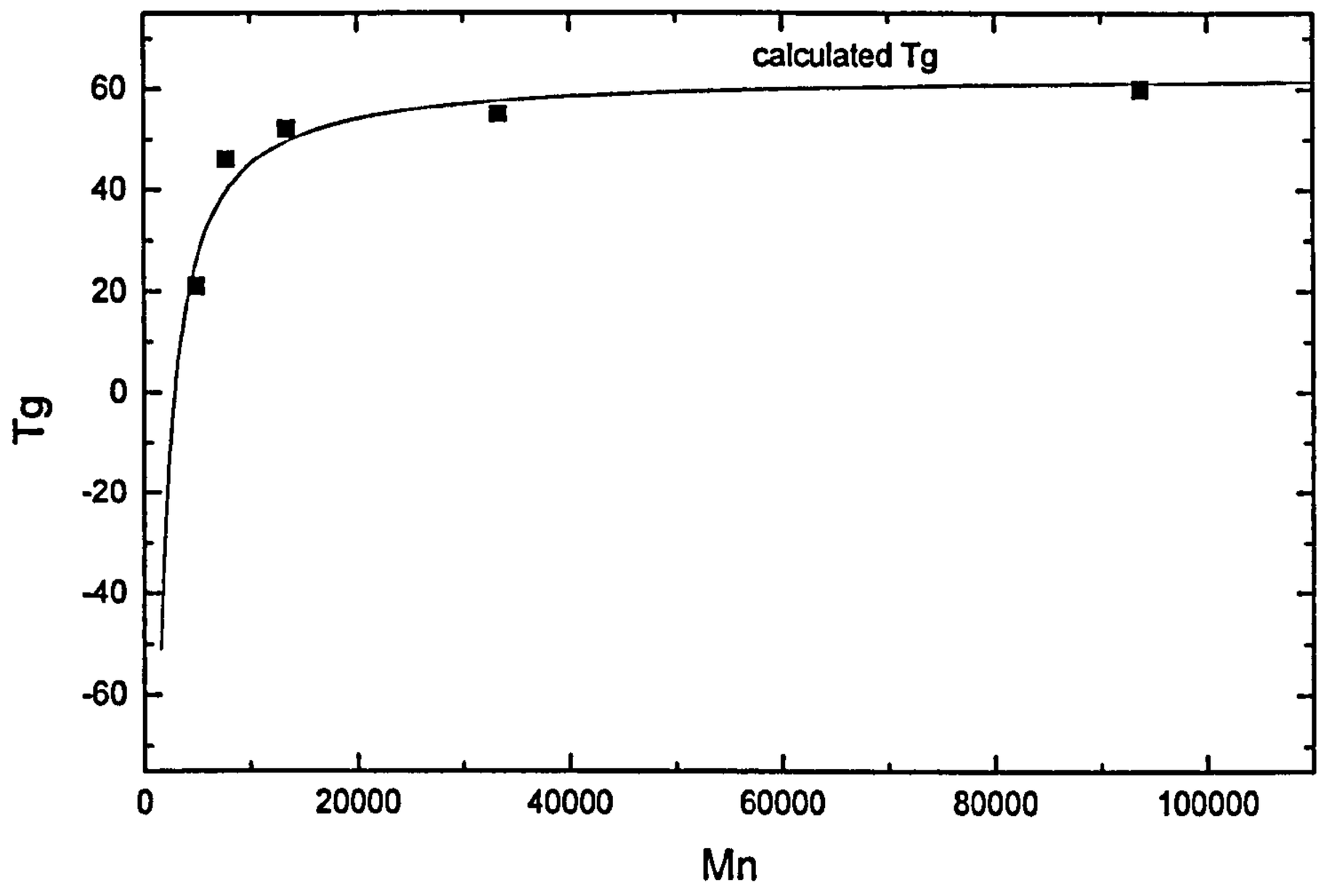

Figure 2.37 – *Predicted glass transition temperature (onset temperature) and experimental values versus M_n graph for MMA/BMA copolymers.*

Equation (2.1) was used again to fit the data for the MMA/BMA co-polymers. The linear least squares analysis gave a $T_{g,\infty}$ value of 336 K (63 °C) and a K value of 1482. Again the T_g data fitted M_n better than the M_w.

Reaction	M_n	M_w	Tg (°C) Onset	Tg (°C) inflection
B1	7820	28300	10	23
B2	11300	38400	18	24
B3	64400	162000	30	34
B4	45200	104000	27	34
B5	191000	414000	30	37

Table 2.9 – *DSC results data for BMA polymers*

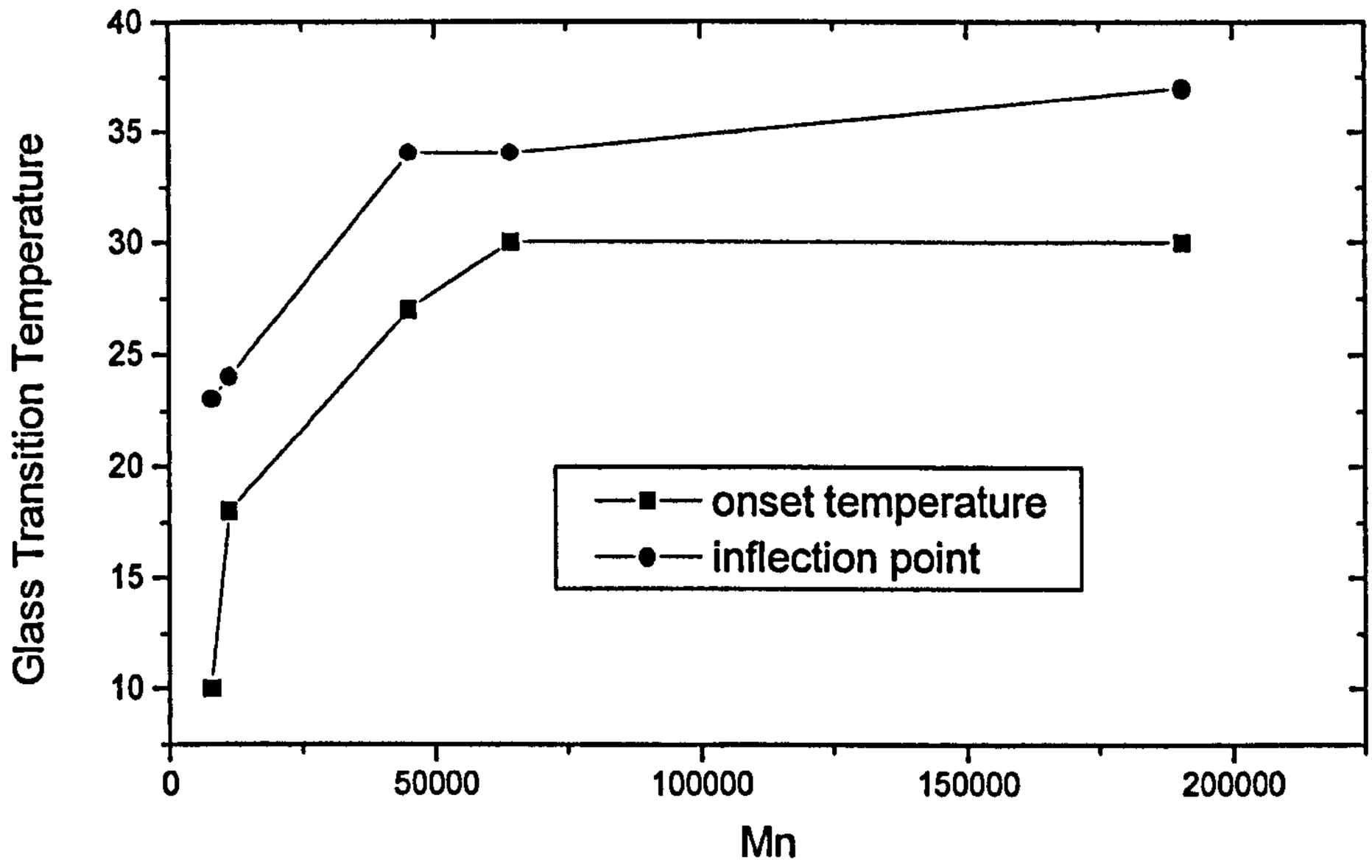

Figure 2.38 – *Glass transition temperature versus M_n for BMA polymers*

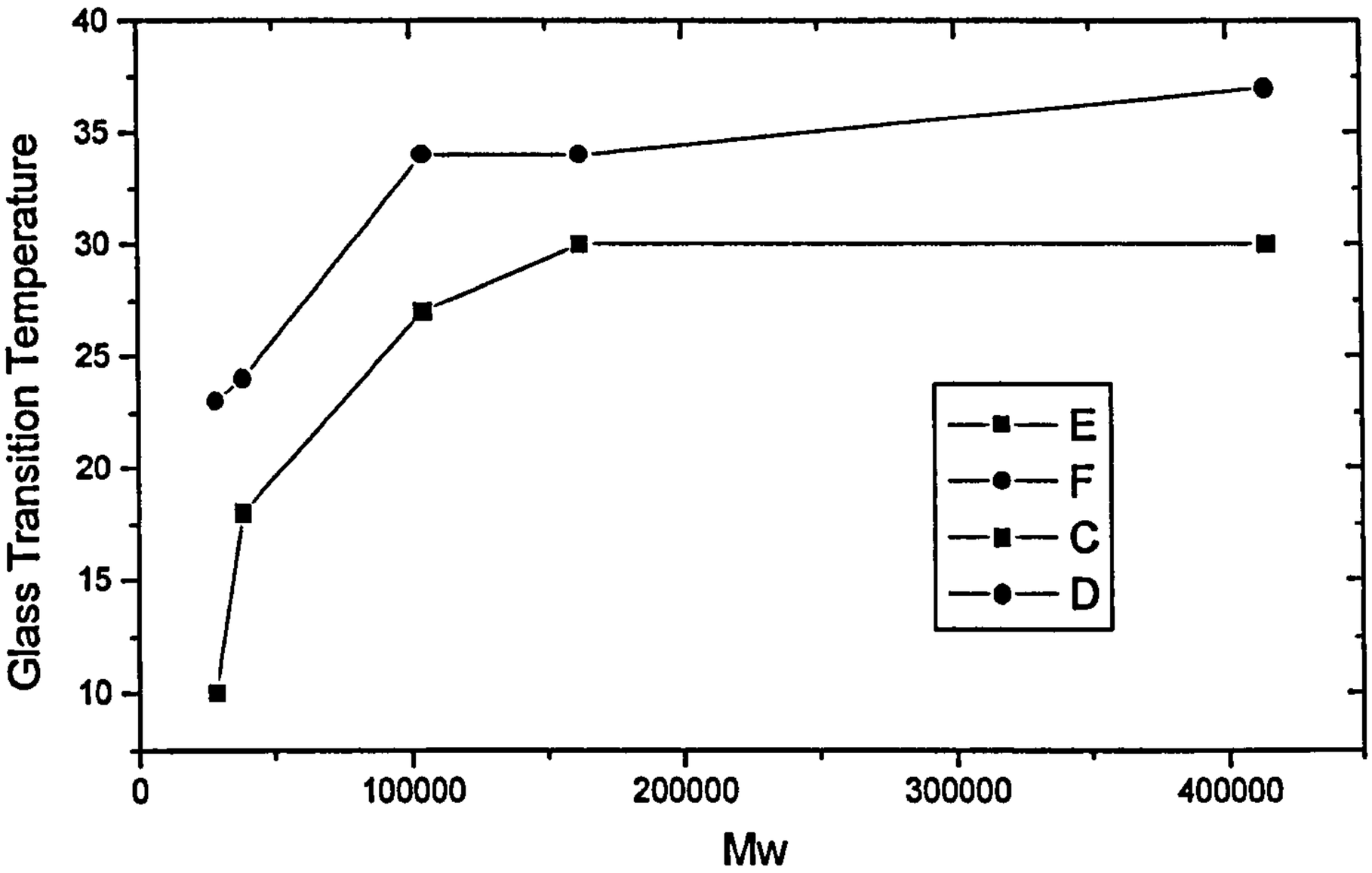

Figure 2.39 – *Glass transition temperature versus M_w for BMA polymers*

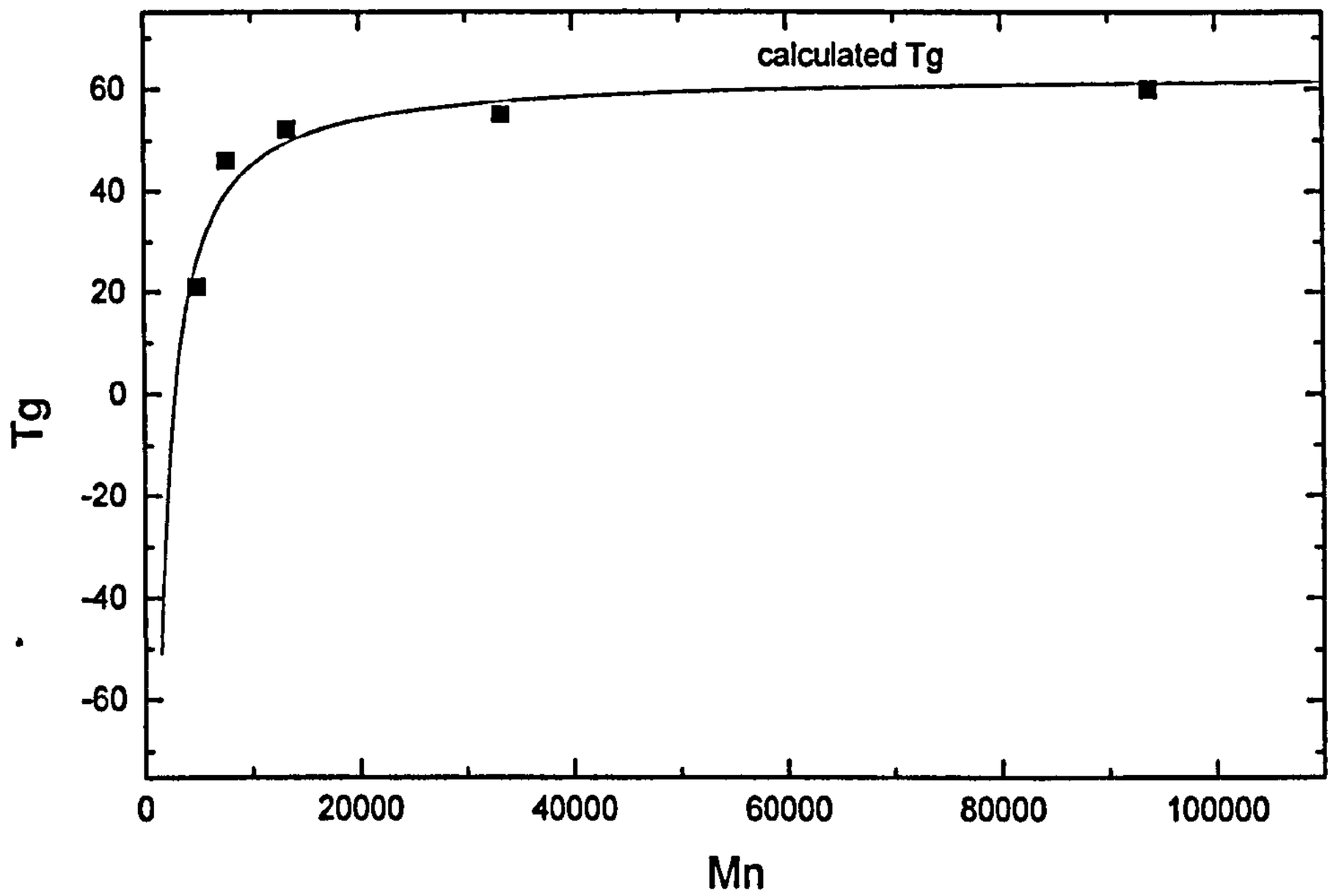

Figure 2.40 – *Predicted onset glass transition temperature versus M_n for BMA polymers (with experimental data shown as squares)*

Performing the linear least squares analysis on the data for the BMA polymers it was found that values for equation 2.1 of $T_{g\infty}$ = 304 K (31°C) and a K value of 1144 best fitted the data.

2.4.2 TGA Analysis of PMMA Polymers

Thermal gravimetric analysis (TGA) is a technique that is used to assess the thermal stability of polymer samples. The instrument consists of a very accurate balance and a sample holder that can be heated to an accurate temperature. The sample is heated at a set heating rate and the weight loss of the sample is measured. Information on the structure of the polymer may be obtained by looking at the resulting trace of weight loss versus temperature. An example TGA trace is shown in figure 2.41.

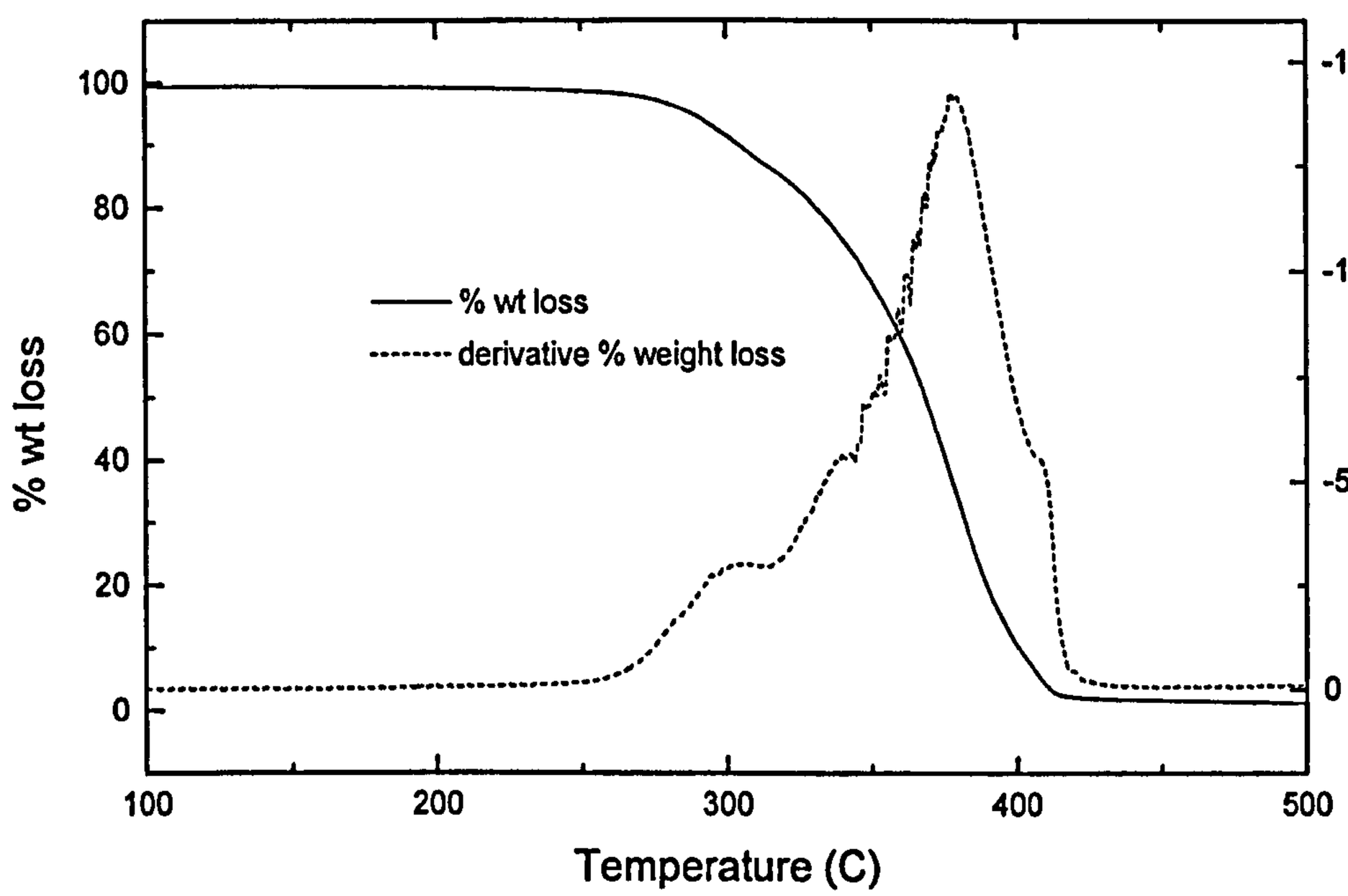

Figure 2.41 – *TGA trace for MMA polymer synthesised in reaction M2*

It is often useful to differentiate the trace from the TGA so transitions can be more clearly observed and the differential trace is overlayed with the standard TGA trace in figure 2.41.

Figure 2.42 compares the different thermal behaviour of PMMA made by CCT polymerisation in emulsion and high molecular weight polymer made with the absence of transfer agent.

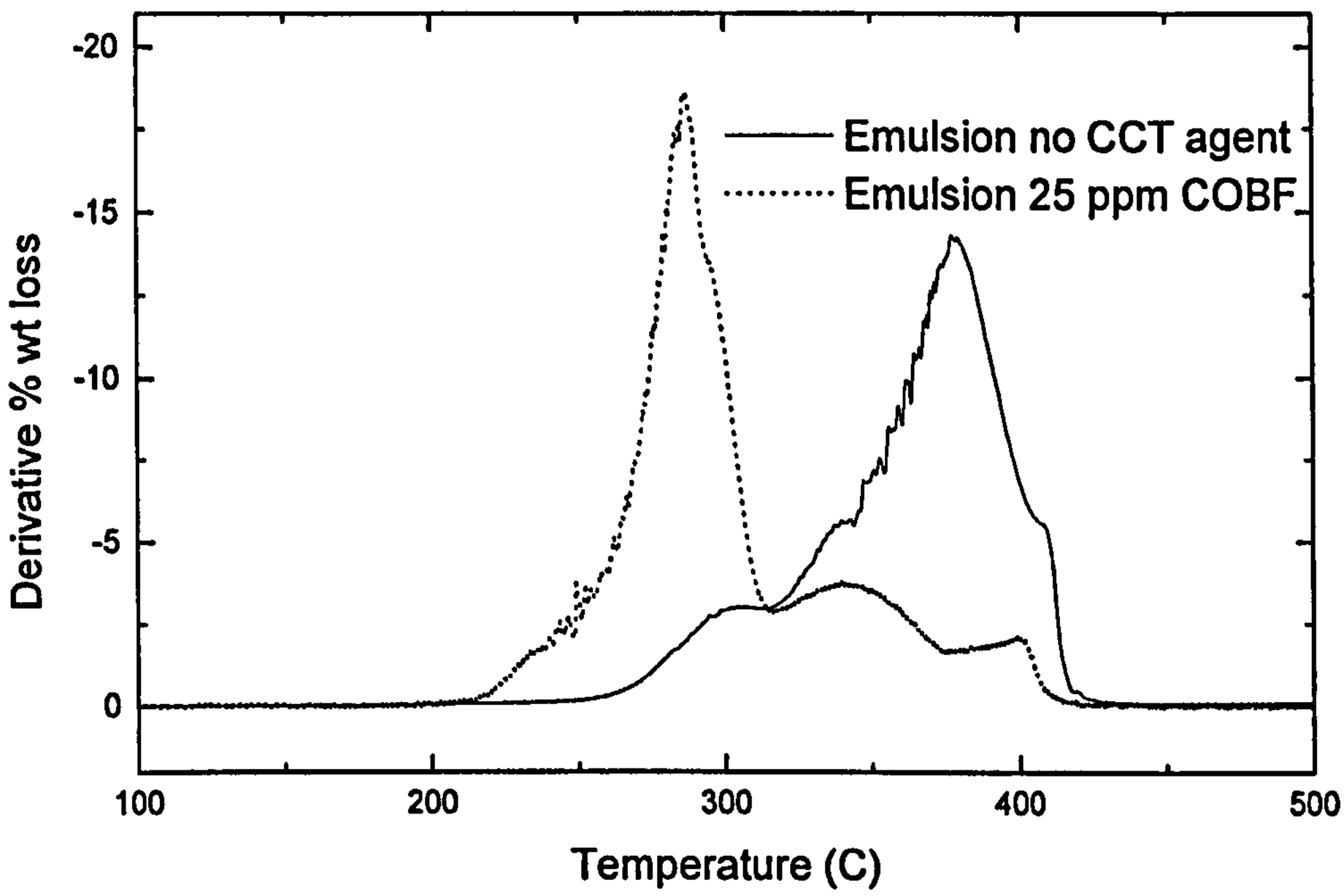

Figure 2.42 – *TGA traces for MMA polymers synthesised in emulsion (M2 and M6)*

The low molecular weight sample is much more thermally unstable than the high molecular weight polymer. At 300°C a significant amount of the low molecular weight polymer has decomposed whereas for the polymer made with the abscence of CCT agent only a fraction of the polymer's weight has been lost. It

has been shown that the unsaturated molecules in a PMMA sample degrade at 230-300°C and the saturated parts decomposes between 300 and 400°C[12-16]. These observations would seem to suggest that some of the polymer made by CCT was terminated with saturated endgroups. The NMR analysis of the polymer made in polymerisation M2 showed that ~92% of the polymer was terminated by vinyl endgroup which again supports the speculation that perhaps not all of the polymer chains made in this CCT polymerisation are terminated by vinyl endgroups. It has been shown that head to head polymer linkages for PMMA lead to degradation at less than 200°C. The absence of any weight loss under 200°C means that there is no observed head to head linkages formed by these emulsion polymerisations.

It is postulated that the degradation of unsaturated PMMA occurs via a β-scission reaction and subsequent unzipping of the polymer chain[14].

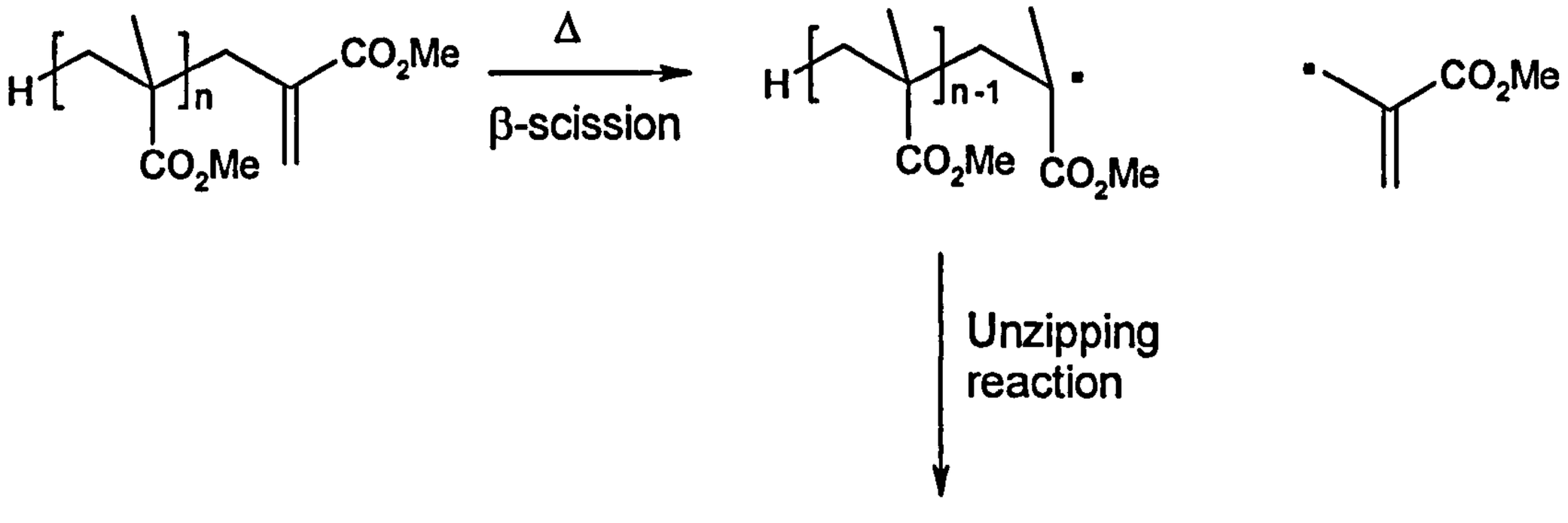

Figure 2.43 – *Thermal decomposition behaviour of PMMA*

It has also been suggested by Manring[14] that unsaturated PMMA degrades by radical addition to the double bond and then the unzipping occurs.

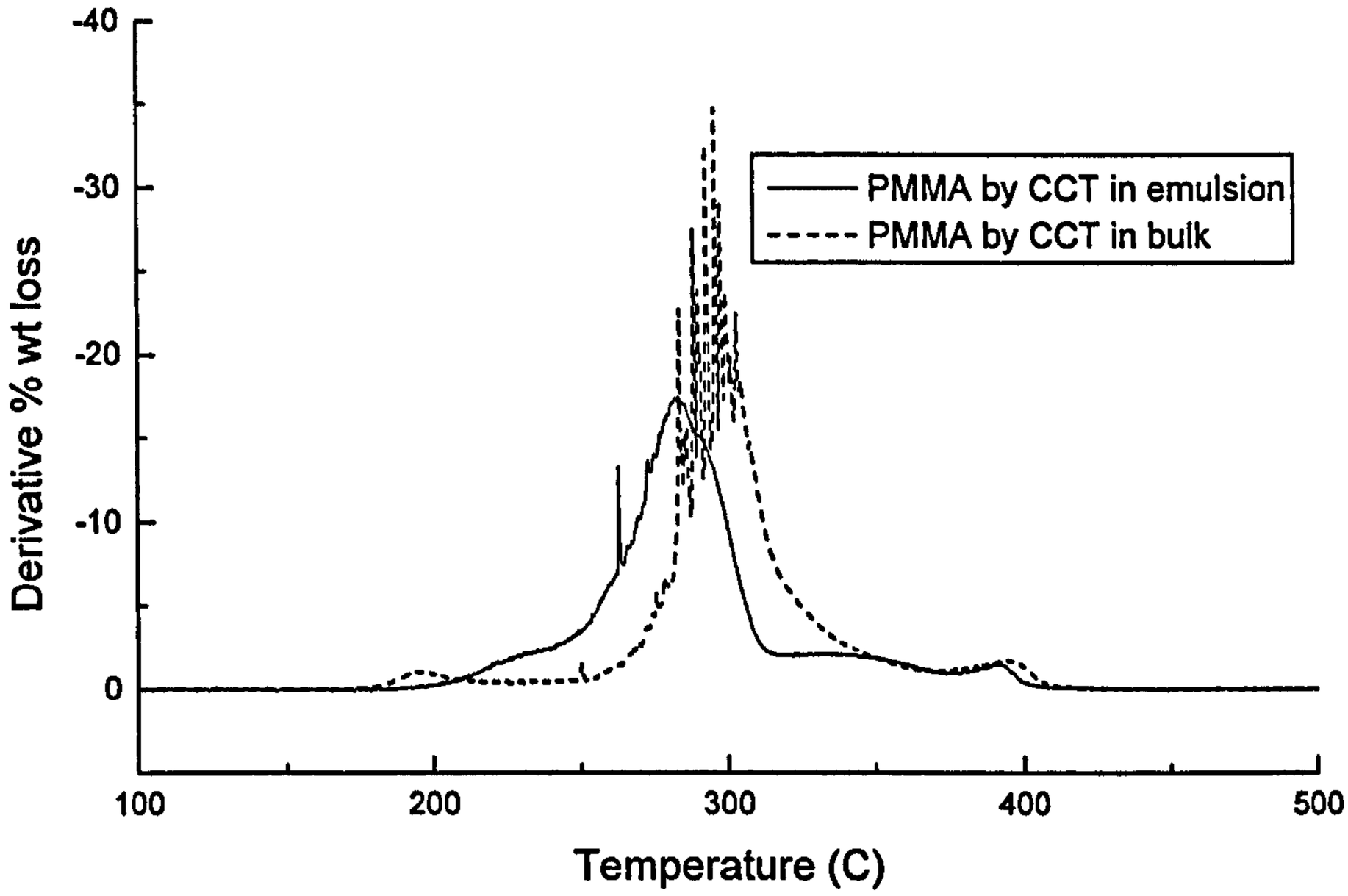

Figure 2.44 – *Thermal decomposition behaviour of PMMA made in bulk and emulsion*

It can be seen that the degradation of the PMMA made by CCT in bulk is quite similar to that made in emulsion. The molecular weights of the polymers used are approximately the same (M_n~3000) and this shows that there is little difference in the thermal behaviour of the polymers.

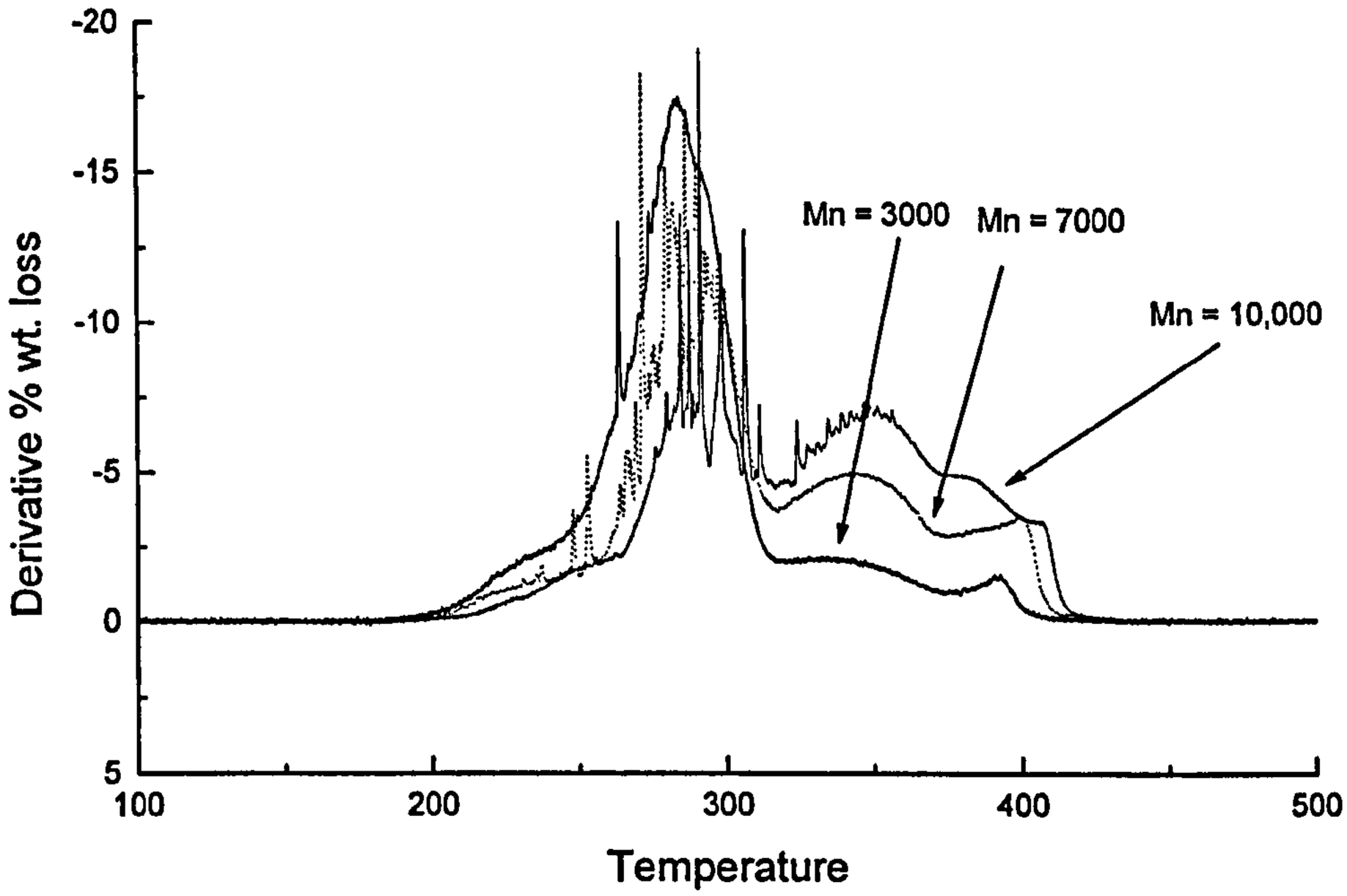

Figure 2.45 – *TGA analysis of PMMA of different molecular weights*

Figure 2.45 shows the effect of molecular weight on the thermal stability of the polymer. As the molecular weight increases the polymer becomes more stable to degradation. It has been published that for unsaturated PMMA samples that degradation is molecular weight independent but the results shown above in figure 2.45 show that although the polymer degrades at the same temperature for all the samples the percentage weight loss under 300 °C is lower the higher the molecular weight. This observation would suggest that as the concentration of CCT agent is reduced there is a greater probability of conventional radical termination events occuring leading to saturated endgroups.

2.5 Conclusions

This chapter has explored the synthesis of alkyl methacrylate macromonomers by CCT emulsion polymerisation. It has been shown that the effective synthesis of certain alkyl methacrylate macromonomers using catalyst concentrations below a threshold level is not possible since the viscosity in the particles becomes too high to allow efficient movement of the CCT agent between latex particles. It has been further demonstrated that an addition of a shot of monomer at the start of the reaction has the effect of reducing the viscosity in the particles allowing effective CCT to occur. The shot of monomer was observed to be less useful for the synthesis of butyl methacrylate macromonomers possibly due to the polymerisations being under starved fed conditions when effective CCT is observed.

This chapter also described the thermal behaviour of the methacrylate polymers synthesised. The glass transition of the polymer was found to be proportional to molecular weight at low chain lengths consistent with previously published results. Also outlined in this chapter was the thermal gravimetric analysis of methyl methacrylate polymers and results shown suggest that perhaps under 100% of polymer chains are terminated by vinyl endgroup for CCT emulsion polymerisations.

2.6 References

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Chapter 3

Synthesis of Co-polymers by CCT Emulsion Polymerisation

3.1 Introduction

The synthesis of co-polymers is of great commercial interest as it allows the chemist to tailor the properties of a polymer product. By polymerising a mixture of two or more monomers in a radical polymerisation it is possible to obtain materials with a wide range of properties. Polymer characteristics such as glass transition temperature and mechanical strength can be tuned to yield materials with specific properties for a required end product.

Co-polymerisation with catalytic chain transfer has been shown to yield *macromonomers* comprising a mixture of monomer units in the chain[1-5]. Work carried out by Gruel et al. was performed in order to see if MMA and styrene had different tendencies to undergo catalytic chain transfer under co-polymerisation conditions[1]. The results indicate that the fraction of unsaturated styrene endgroups is directly proportional to the fraction of styrene monomer used in the polymerisation feed, this result was supported by work carried out by Heuts et al[3]. Other related work looked at the tendency of α-methylstyrene (AMS) to co-polymerise with styrene under CCT conditions[2]. It was found that even at low AMS concentrations the majority of polymer chains were terminated with an

AMS endgroup. This result was thought to be due to the high transfer constant observed with the AMS and also its very low rate of propagation i.e. once an AMS group had added onto the end of a polymer chain it was more likely to undergo CCT than propagate.

Work undertaken to look at the co-polymerisation of MMA and styrene using catalytic chain transfer emulsion polymerisation was carried out by Suddaby et al.[4]. A compositional drift through the course of the polymerisation was found (as would be expected) and also on the addition of the styrene the overall observed chain transfer constant was reduced compared to pure MMA (since styrene has a lower transfer constant than the MMA).

The research described in the following chapter describes the synthesis of co-macromonomers (i.e. macromonomers with more than one type of monomer in the chain) by catalytic chain transfer emulsion polymerisation.

3.2 CCT Emulsion Polymerisation of MMA/HEMA

The use of the readily available water soluble monomer hydroxyethyl methacrylate (HEMA) in a polymerisation allows the simple incorporation of hydroxyl groups into a polymer. Hydroxyl groups are very useful groups to include into polymers as they allow the possibility of functionalising the polymer by quite simple hydroxyl transformation. Since HEMA is a methacrylate it is able to be used in *catalytic chain transfer* polymerisation and so the work described in this section was carried out to synthesise macromonomers

incorporating HEMA units by CCT emulsion polymerisation. Methyl methacrylate was chosen as a co-monomer since MMA is a hydrophobic monomer and allows the formation of stable latex particles.

Figure 3.1 is the product that should be formed by performing *catalytic chain transfer* polymerisation on a mixture of MMA and HEMA.

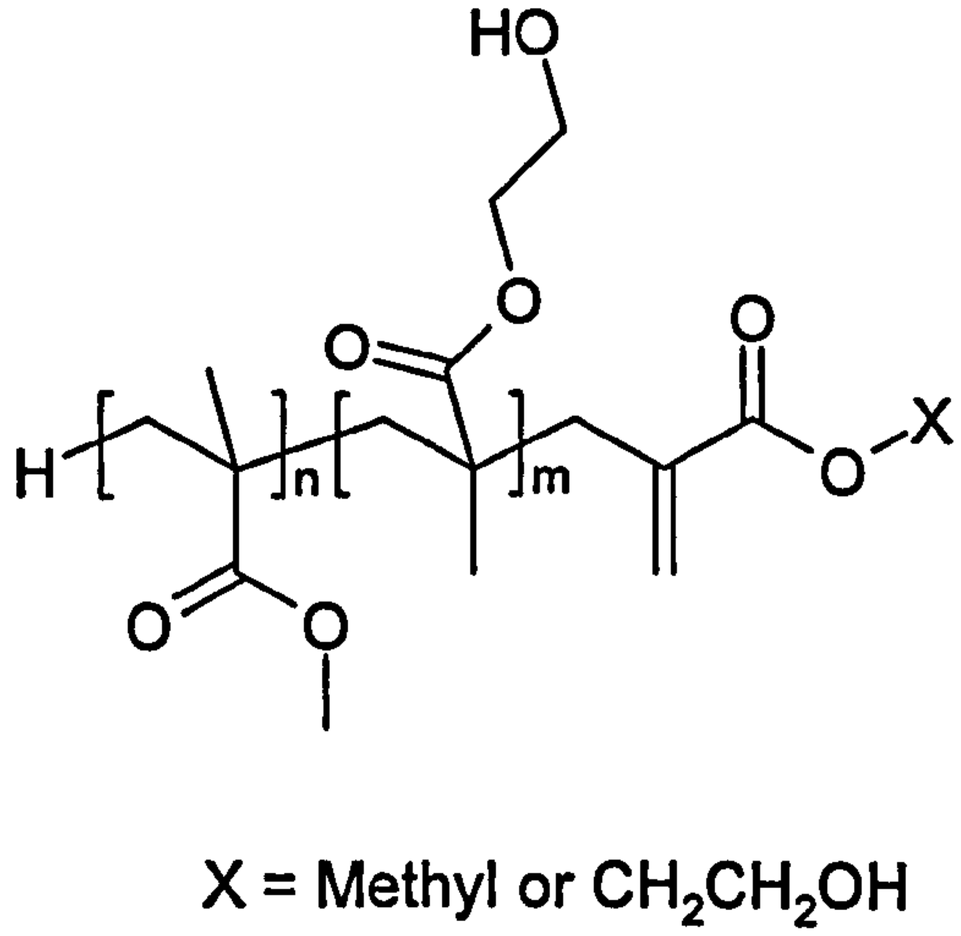

Figure 3.1 – *Structure of MMA/HEMA statistical macromonomer*

3.2.1 MMA/HEMA 70:30 molar ratio

The data shown in table 3.1 suggests that the successful synthesis of MMA-*co*-HEMA macromonomers has been achieved under emulsion polymerisation conditions. Since both monomers are methacrylates and hence similar in structure the reactivity ratios r_1 and r_2 will be both be roughly equal to one and there will be no observed compositional drift.

Reaction	Wt. COBF (g)	Ppm COBF	Feed Conditions	Mn	PDi	Inst. Conv.	Cs^E
MH1	0.040	45.23	100% fed	1850	1.48	1.022	1302
MH2	0.028	35.54	100% fed	2540	1.72	1.016	1209
MH3	0.024	30.19	100% fed	2730	1.61	1.017	1323
MH4	0.020	19.54	100% fed	16600	1.98	1.032	336
MH5	0.009	11.77	100% fed	25200	2.02	1.039	367
MH6	0.009	11.77	20% shot/ 80% fed	7780	1.75	0.983	1187

Table 3.1 - *End properties of MMA/HEMA (70:30) CCT polymerisations in emulsion*

The example NMR in figure 3.2 (final polymerisation product for reaction MH1) clearly shows that macromonomer has been formed containing both MMA and HEMA repeat units. The assignment of the NMR peaks is given in table 3.2.

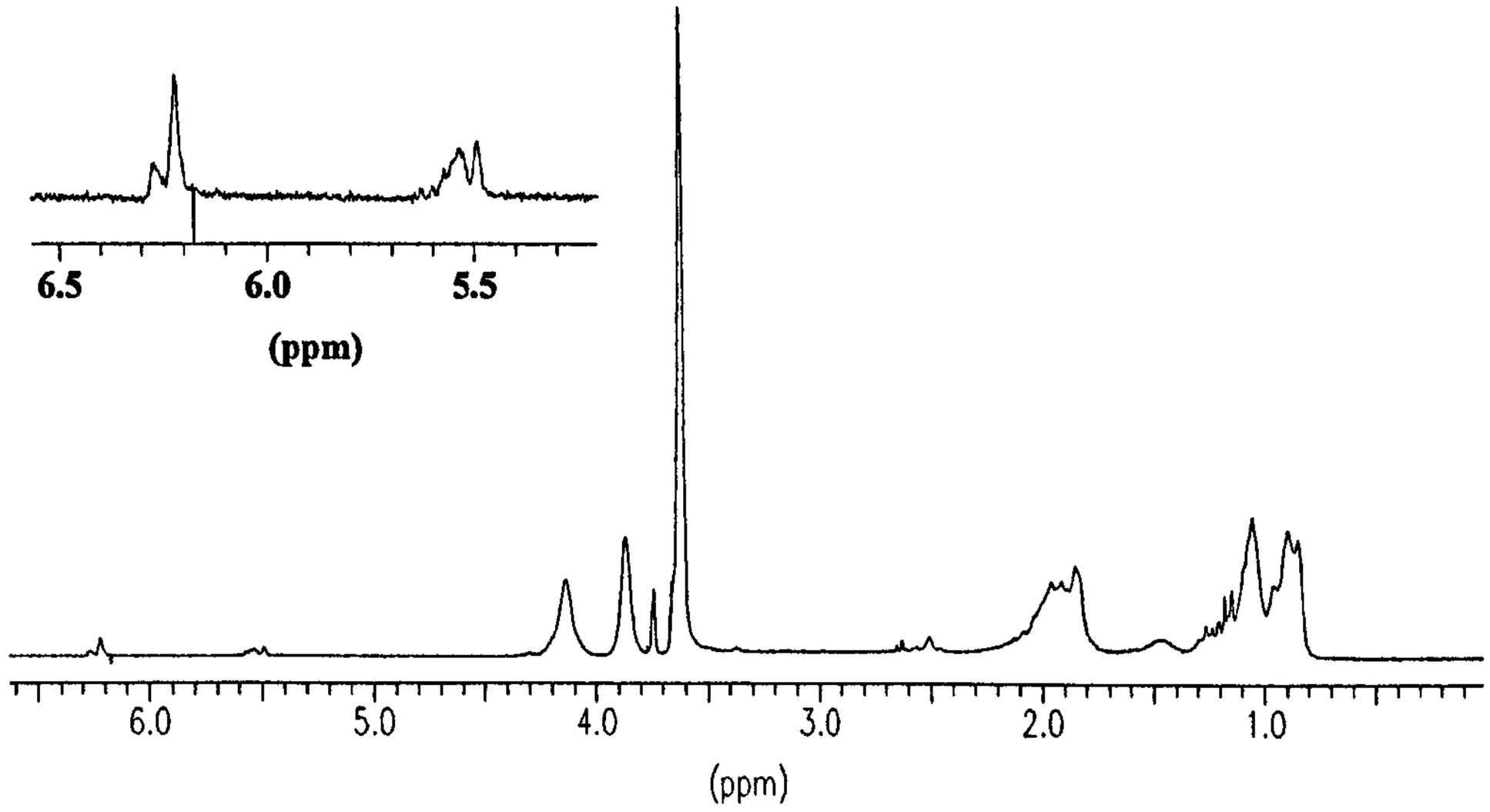

Figure 3.2 – *^{1}H NMR spectrum of MMA/HEMA statistical macromonomer synthesised by CCT emulsion polymerisation MH1.*

In the CCT polymerisation of MMA and HEMA, both may undergo CCT reaction and so in the final polymer product there will be a mixture of endgroups. The terminus of the polymer will depend upon whether the chain transfer reaction has occurred with a MMA unit or a HEMA unit.

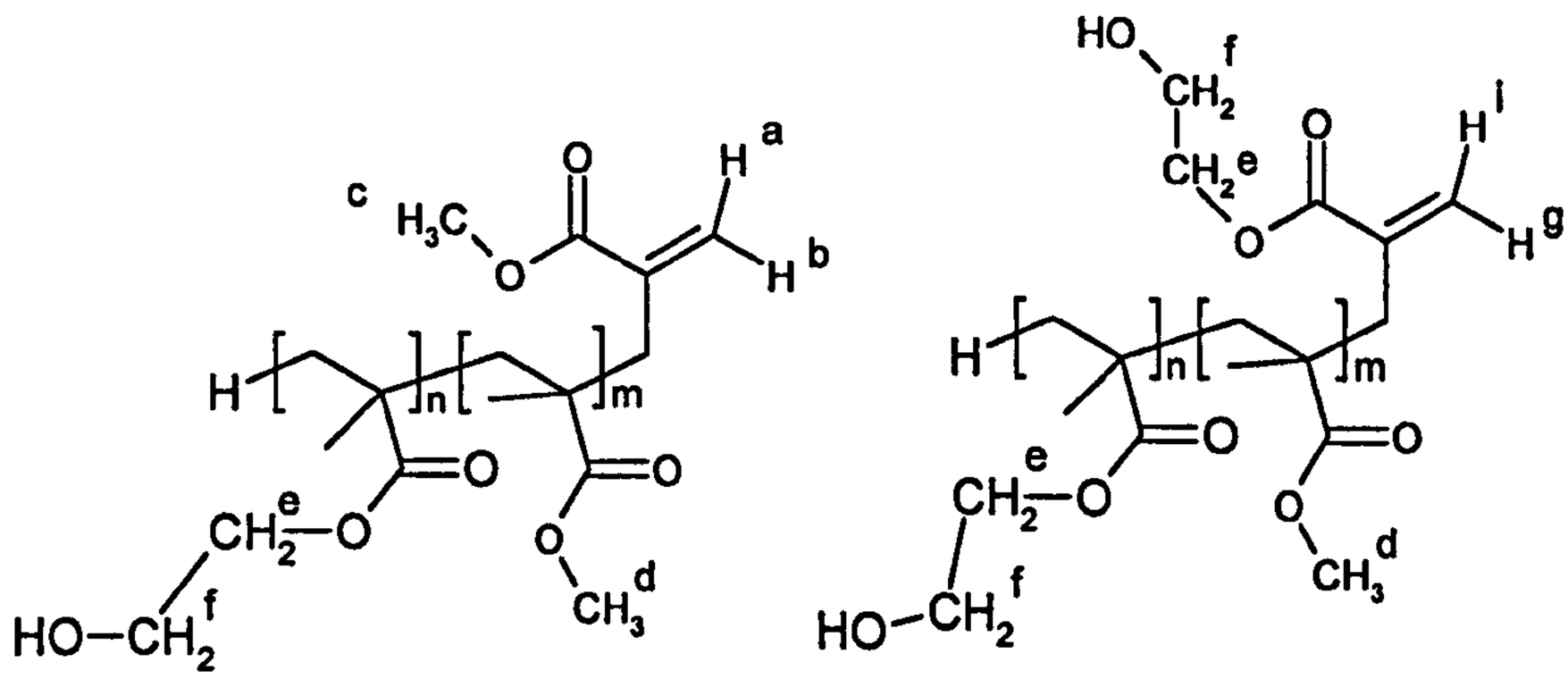

Figure 3.3 – *Structure of MMA/HEMA macromonomer with protons labelled for NMR analysis.*

Peak (ppm)	Integral	Multiplet Type	Assignment
6.25	1.00	2 x singlet	Vinyl protons [a] and [i]
5.51	1.00	2 x singlet	Vinyl protons [b] and [g]
4.14	11.16	singlet	O-CH_2 proton [e]
3.87	11.25	singlet	O-CH_2 proton [f]
3.74	42.44	singlet	Terminal methoxy proton [c]
3.62		singlet	Remaining methoxy protons [d]
0.5 - 3.5	109.61	multiplets	In chain CH_2 and CH_3 protons

Table 3.2 – *Assignment of peaks for NMR spectrum in figure 3.2*

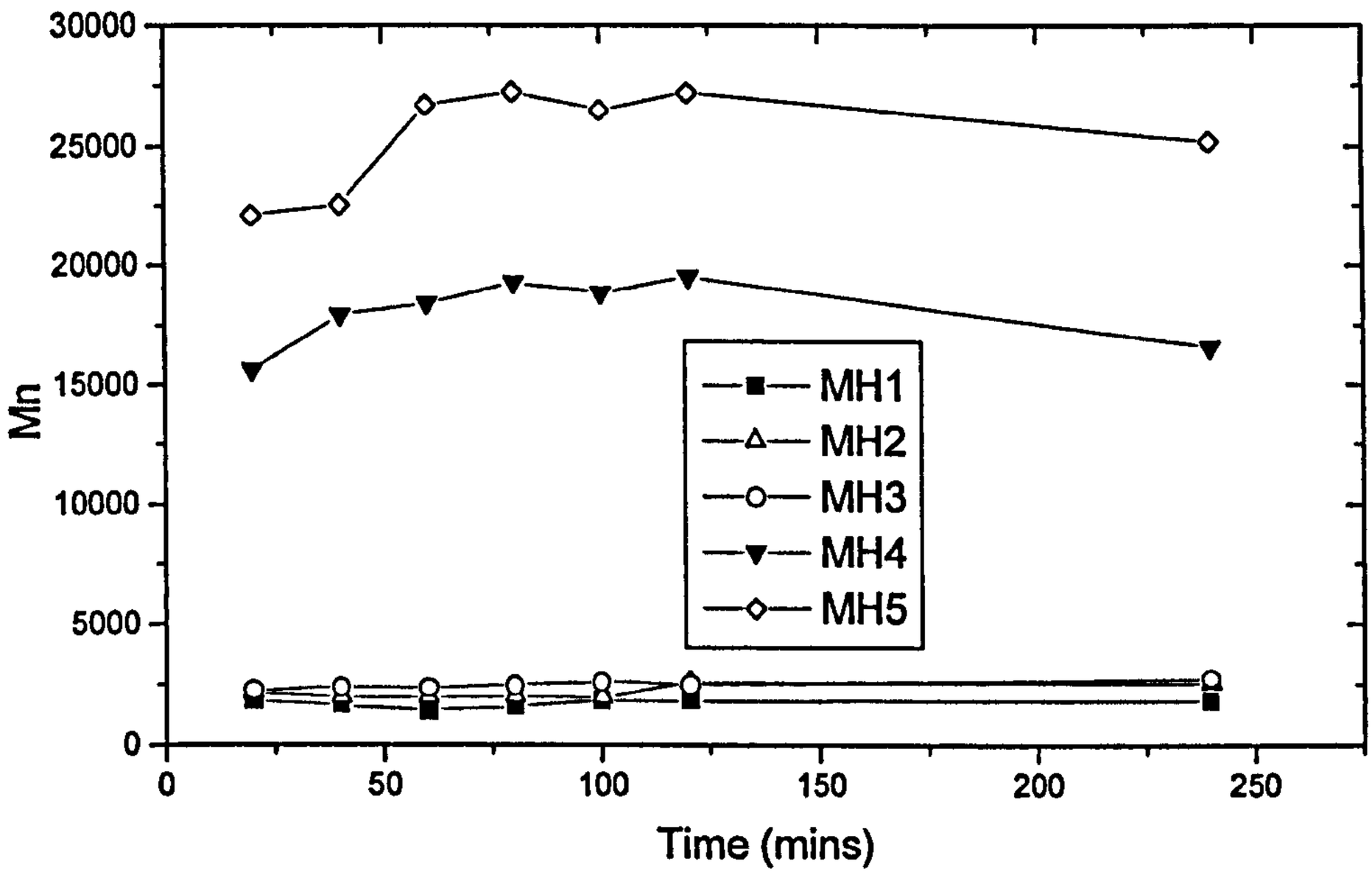

Figure 3.4 – *M_n versus time graph for emulsion polymerisations MH1-MH5*

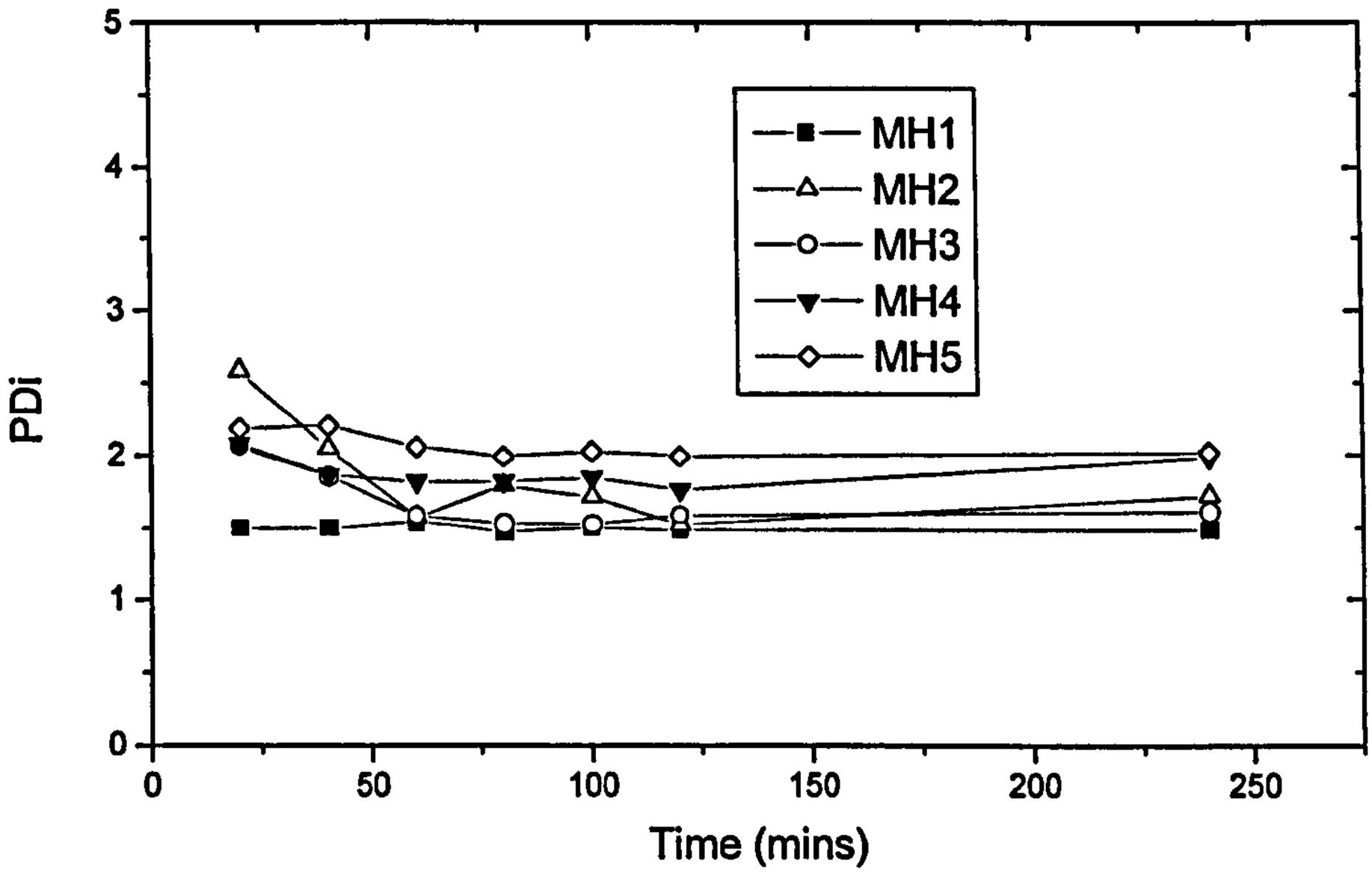

Figure 3.5 – *Polydispersity index versus time graph for emulsion polymerisations MH1-MH5*

Figures 3.4 and 3.5 show the successful synthesis of the MMA/HEMA macromonomers. Reactions MH1-MH3 observe the formation of low molecular weight polymers consistent with effective catalytic chain transfer in emulsion as described in chapter 2. The polydispersity index of all the samples is low (around 2) which is expected for the CCT reaction. Polymerisations MH4 and MH5 exhibit much higher molecular weights than for the other reactions and it can be observed in table 3.1 that the observed effective chain transfer constant (Cs^E) for these reactions is noticeably lower than for reactions MH1-MH3. A Cs^E of around 300 being observed for reactions MH4 and MH5 compared to the Cs^E value of about 1300 for the MH1-MH3 reactions.

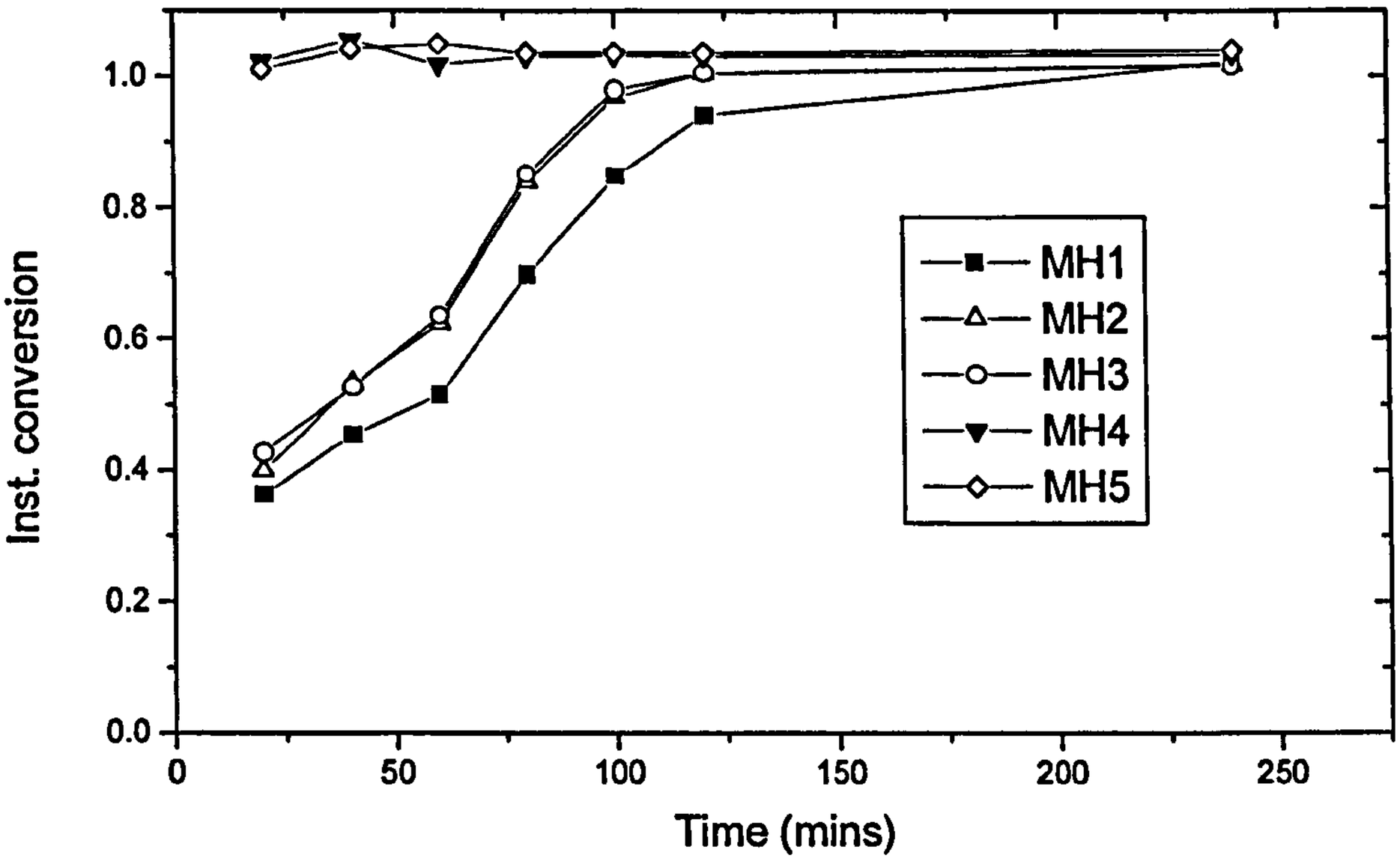

Figure 3.6 – *Instantaneous conversion versus time graph for emulsion polymerisations MH1-MH5*

The instantaneous conversion versus time graph shows that reactions MH1-MH3 exhibit very similar rates of reaction to the pure MMA case (chapter 2) with the emulsion polymerisation proceeding under *non* -starved fed conditions allowing efficient macromonomer synthesis. For reactions MH4 and MH5 the instantaneous conversion is much higher at the early stages of the reaction and the polymerisation is operating under starve fed conditions. It is observed that in the same manner as for the synthesis of pure MMA macromonomers by CCT emulsion polymerisation, that a threshold level of catalyst level is reached, below which the transfer reaction does not proceed efficiently (see section 2.2)

In chapter 2 it was shown that the injection of a shot of 20% of the monomer/catalyst mixture at the start of the reaction allowed effective CCT to be carried out with low levels of catalyst (below ~15 ppm) for MMA and for a

BMA/MMA mixture. The monomer shot had the effect of bring the polymerisation from a starved fed to a non-starved fed state allowing the CCT reaction to proceed at full effectiveness. The monomer shot was not as effective for the synthesis of low molecular weight pure BMA polymers since the reactions for higher concentrations of CCT agent (where efficient chain transfer was observed) appeared to be under starved fed conditions already and hence the monomer shot had little effect.

For the MMA/HEMA polymerisations the reactions with high Cs^E are all at low instantaneous conversions early in the polymerisation and so it is expected that the addition of a monomer shot would allow lower catalyst concentrations to be employed.

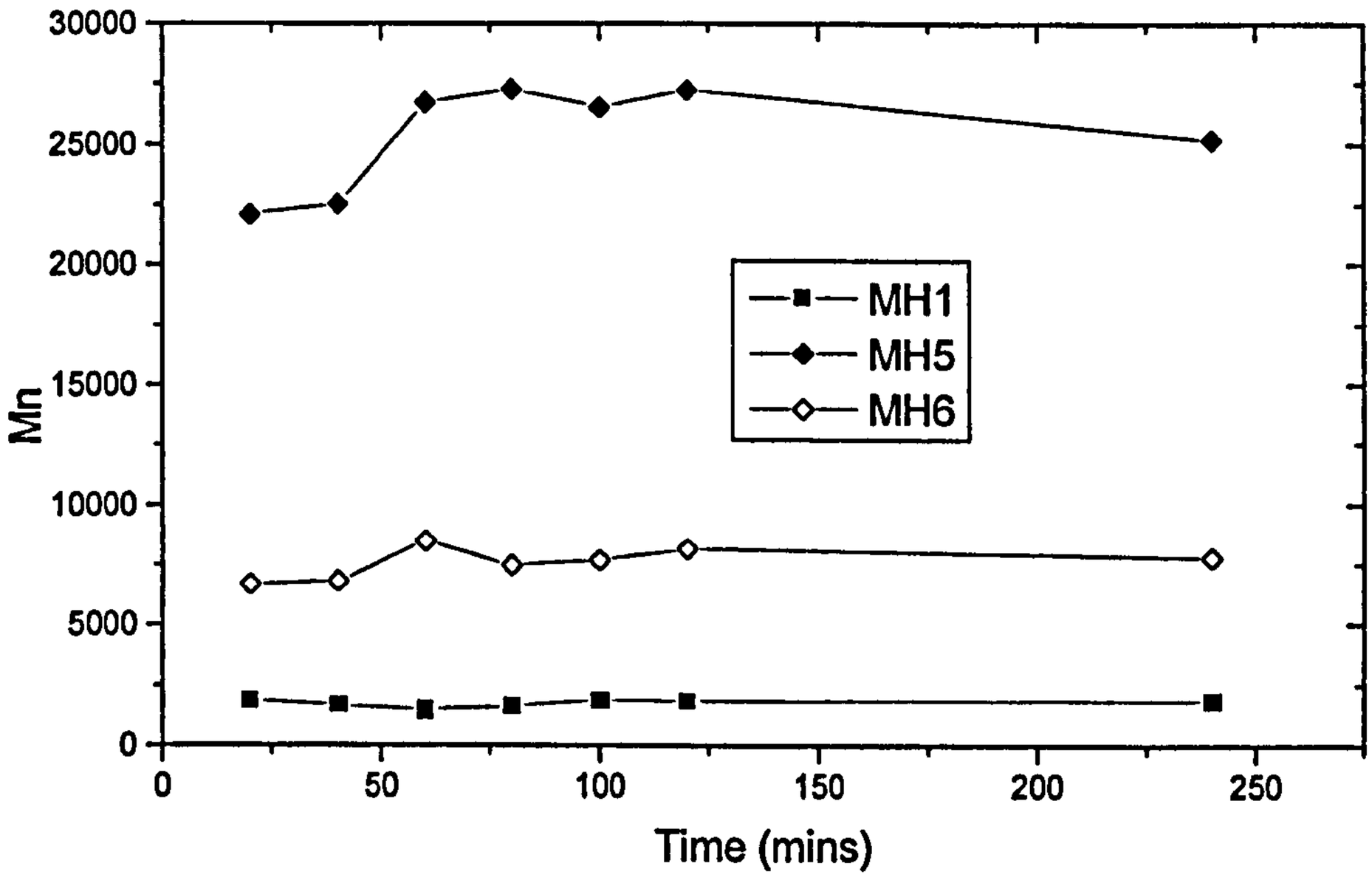

Figure 3.7 - *M_n versus time graph for emulsion polymerisations MH1,MH5 and MH6*

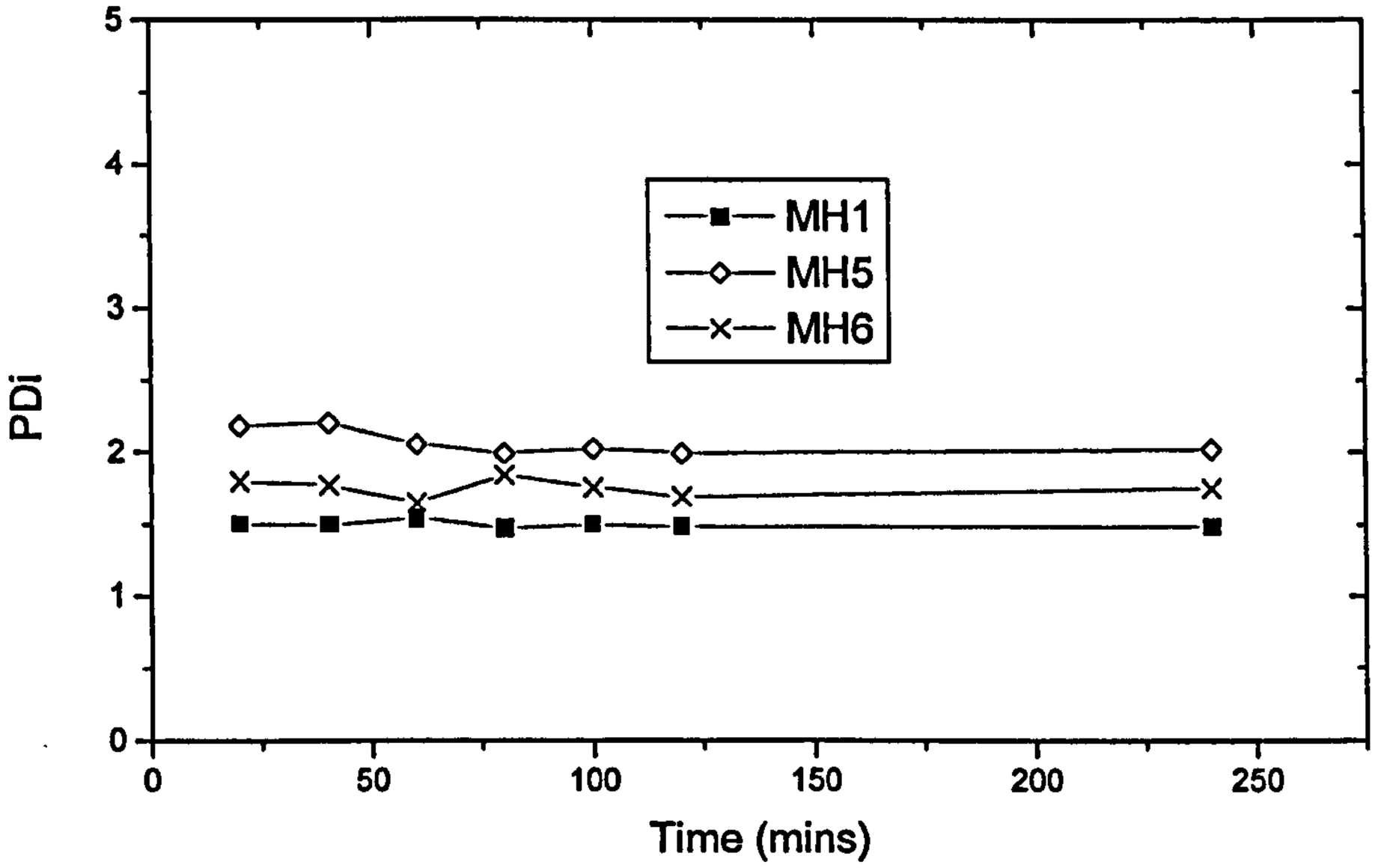

Figure 3.8 – *Polydispersity index versus time graph for emulsion polymerisations MH1, MH5 and MH6*

Figures 3.7 and 3.8 show that the addtion of a 20% shot of monomer / catalyst mixture has allowed the CCT reaction to be carried out at a wider range of catalyst concentrations and hence permitted the synthesis of a wider range of MMA/HEMA co-polymers by this method. It can be seen in figure 3.9, that the experiment where the monomer shot was added (polymerisation MH6) has a much slower rate of polymerisation over the first 100 minutes of polymerisation than for the other experiments with low catalyst levels. The observed reduction in the rate indicates that the monomer shot achieved the change from starve fed to non-starve fed conditions that was desired.

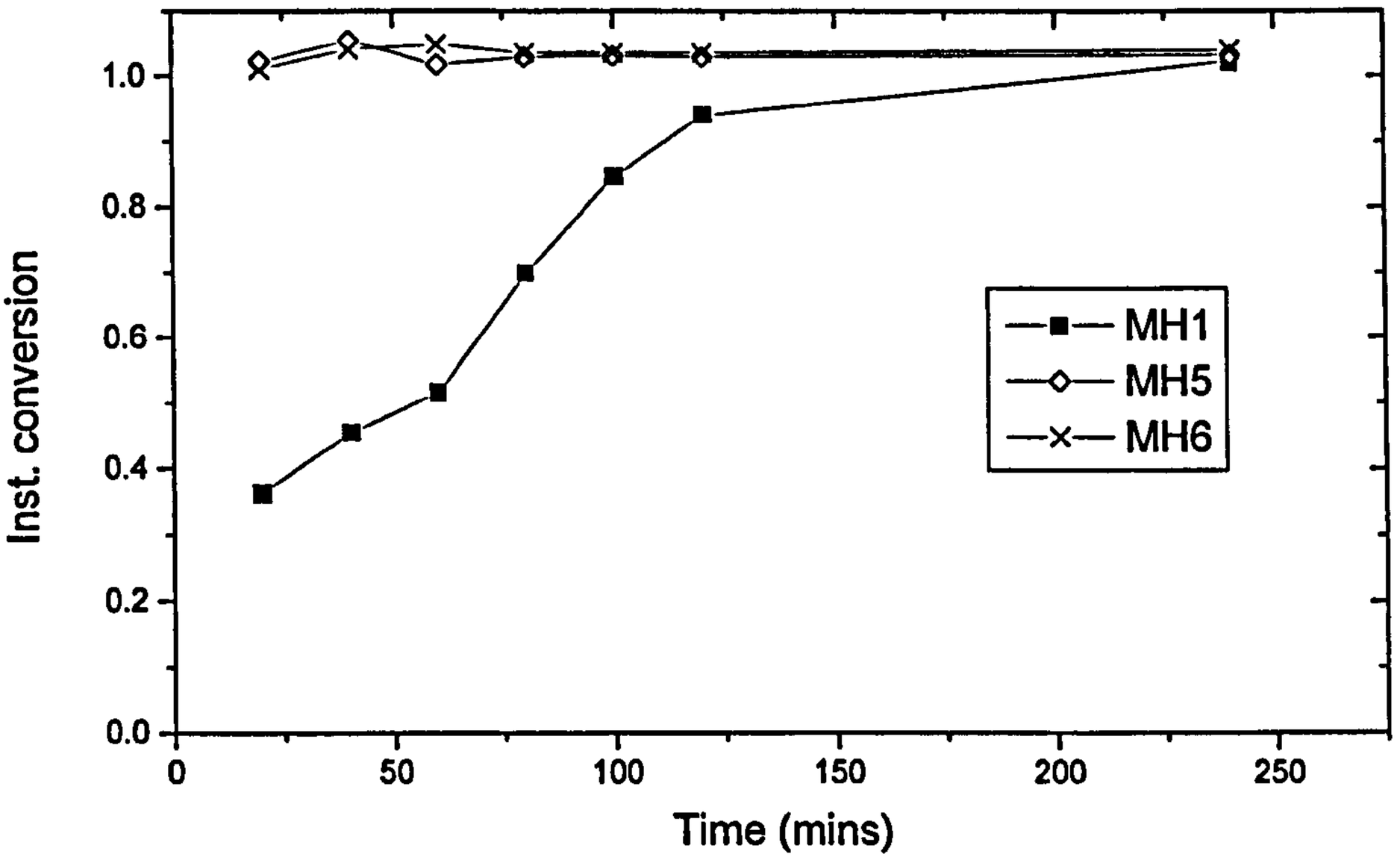

Figure 3.9 – *Instantaneous conversion versus time graph for emulsion polymerisations MH1, MH5 and MH6*

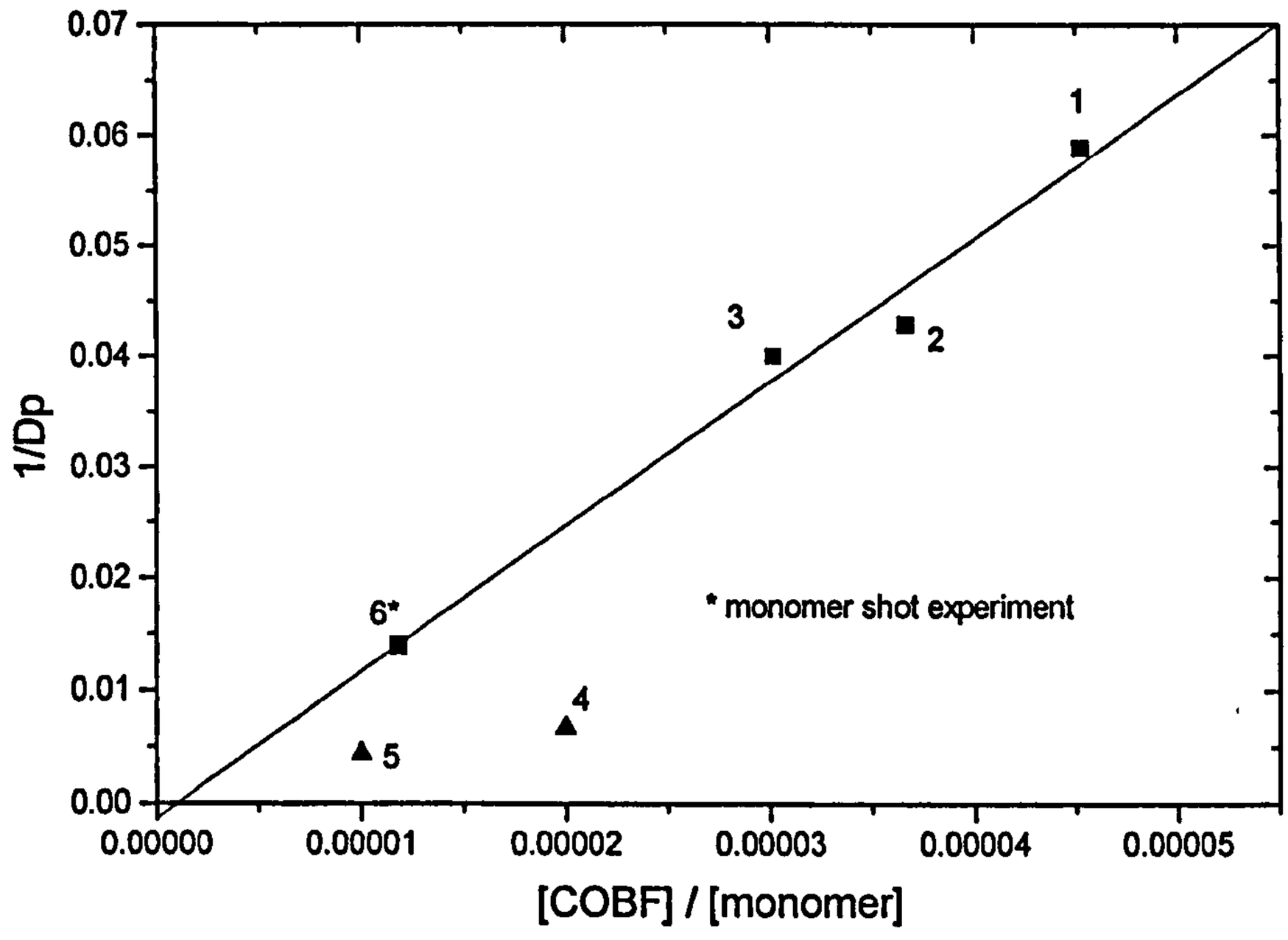

Figure 3.10 – *Pseudo Mayo plot for MMA/HEMA (70:30 molar ratio) emulsion co-polymerisations using COBF as the transfer agent.*

Figure 3.10 shows a *pseudo*-Mayo plot for the MMA/HEMA reactions. It gives a Cs^E (effective chain transfer constant in emulsion) of 1300 which is identical to that for pure MMA.

3.2.1.1 DSC Analysis of MMA/HEMA (70:30 molar ratio) co-polymers

The glass transition temperature of the polymers synthesised in section 3.2.1 were measured using differential scanning calorimetry. The results are shown in table 3.3.

Reaction	M_n	M_w	T_g onset / °C	T_g inflection / °C
MH1	1850	2740	36.0	50.7
MH2	2540	4370	52.3	62.1
MH3	2730	4390	58.6	70.7
MH4	16600	32900	102.7	113.7
MH5	25200	50900	103.9	115.7

Table 3.3 - *DSC results for MMA/HEMA co-polymers synthesised in emulsion polymerisations MH1-MH5*

In chapter 2 it was shown that $T_g = T_{g\infty} - K/D_p$, where $T_{g\infty}$ is the limiting glass transition temperature at high molecular weight and K is a constant value. Using least squares analysis on the glass transition temperatures for MMA/HEMA co-polymers a $T_{g\infty}$ of 383 K (110 °C) and a K constant value of 1281 were obtained.

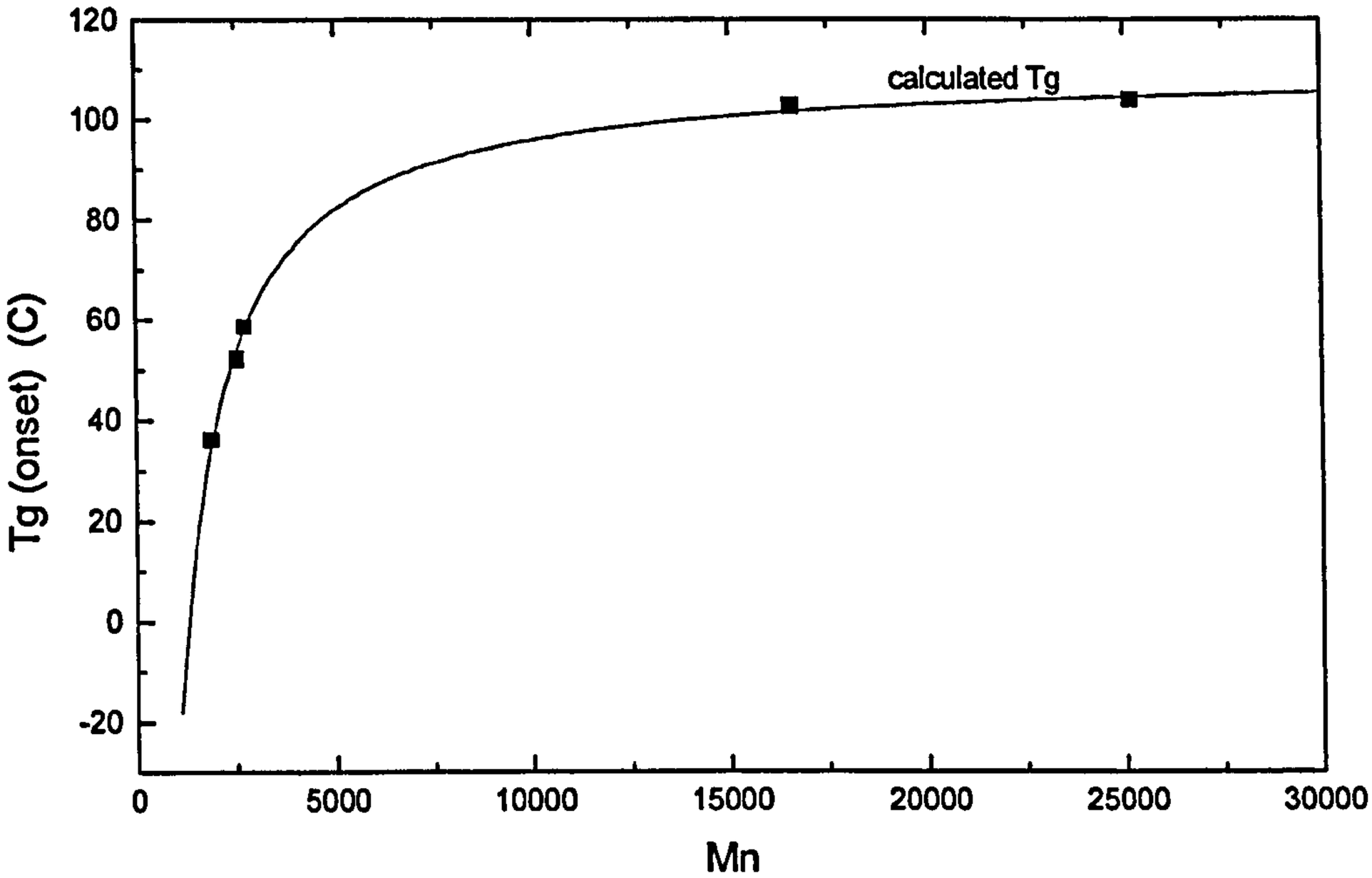

Figure 3.11 – *Glass transition temperature versus M_n for MMA/HEMA co-polymers*

The K and $T_{g\infty}$ values for the MMA/HEMA co-polymers are very close to those for pure MMA macromonomers ($T_{g\infty}$ = 392 K , K = 1205).

3.1.2 MMA/HEMA 50:50 molar ratio

The synthesis of MMA/HEMA macromonomers with a higher amount of HEMA than in section 3.2 was attempted. CCT emulsion polymerisation was carried out on a 50:50 mixture of MMA/HEMA and although effective CCT was observed the emulsion was not stable, with coagulation being observed in the later stages of the reaction.

Reaction	Wt. COBF (g)	Ppm COBF	Feed Conditions	M_n	PDi	Inst. Conv.	Cs^E
MH7	0.028	36.67	100% fed	2070	1.55	1.057	1533

Table 3.4 – *End properties of CCT emulsion polymerisation MH7*

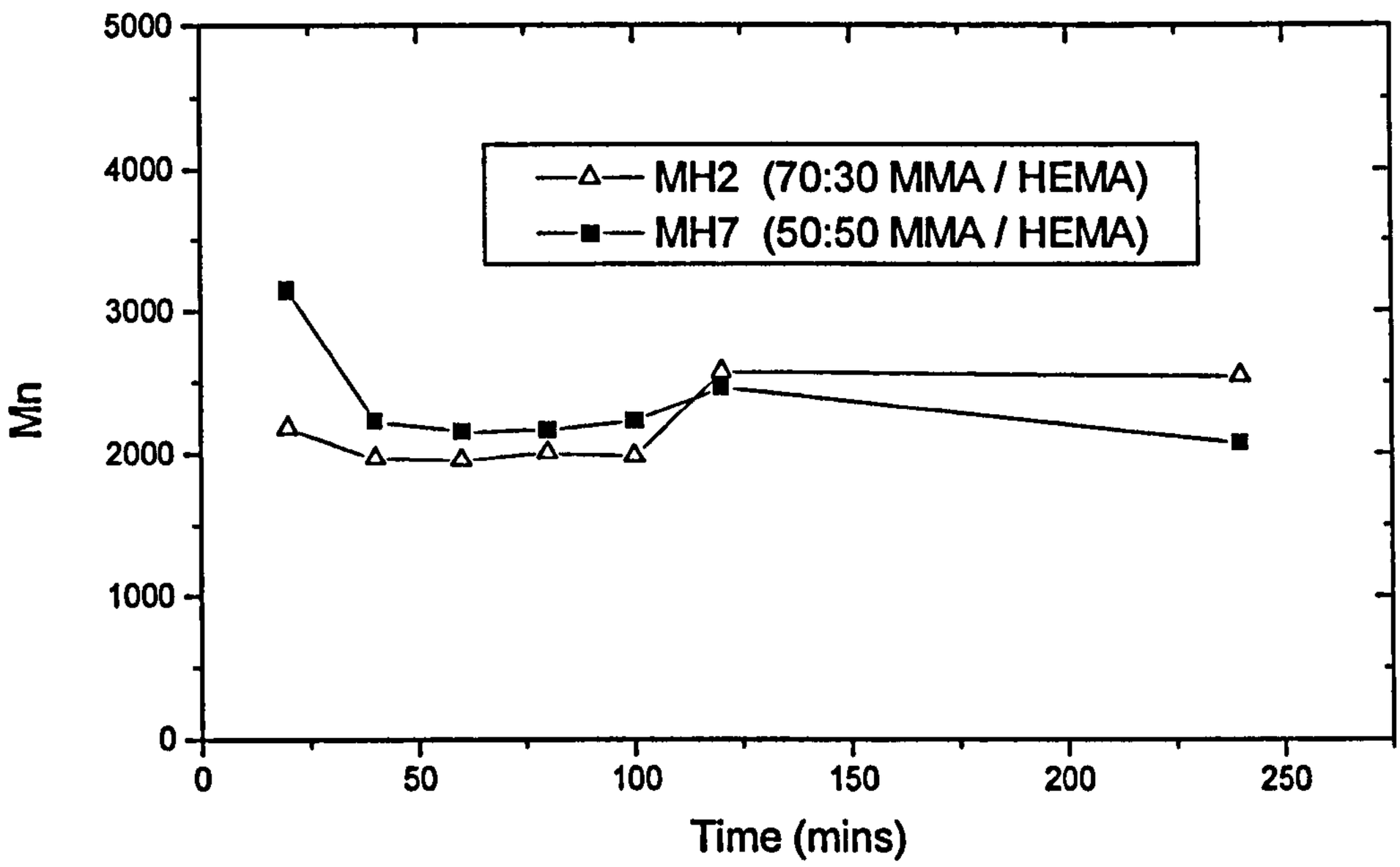

Figure 3.12 – *M_n versus time graph for emulsion polymerisations MH2 and MH7*

It can be seen in figure 3.12 that the molecular weight of the polymer formed in the CCT emulsion polymerisation of a MMA / HEMA mixture is relatively insensitive to the amount of HEMA in the system. Both polymerisations employ approximately the same concentration of CCT agent (moles COBF : moles monomer) and this means that both polymerisations will have similar Cs^E values.

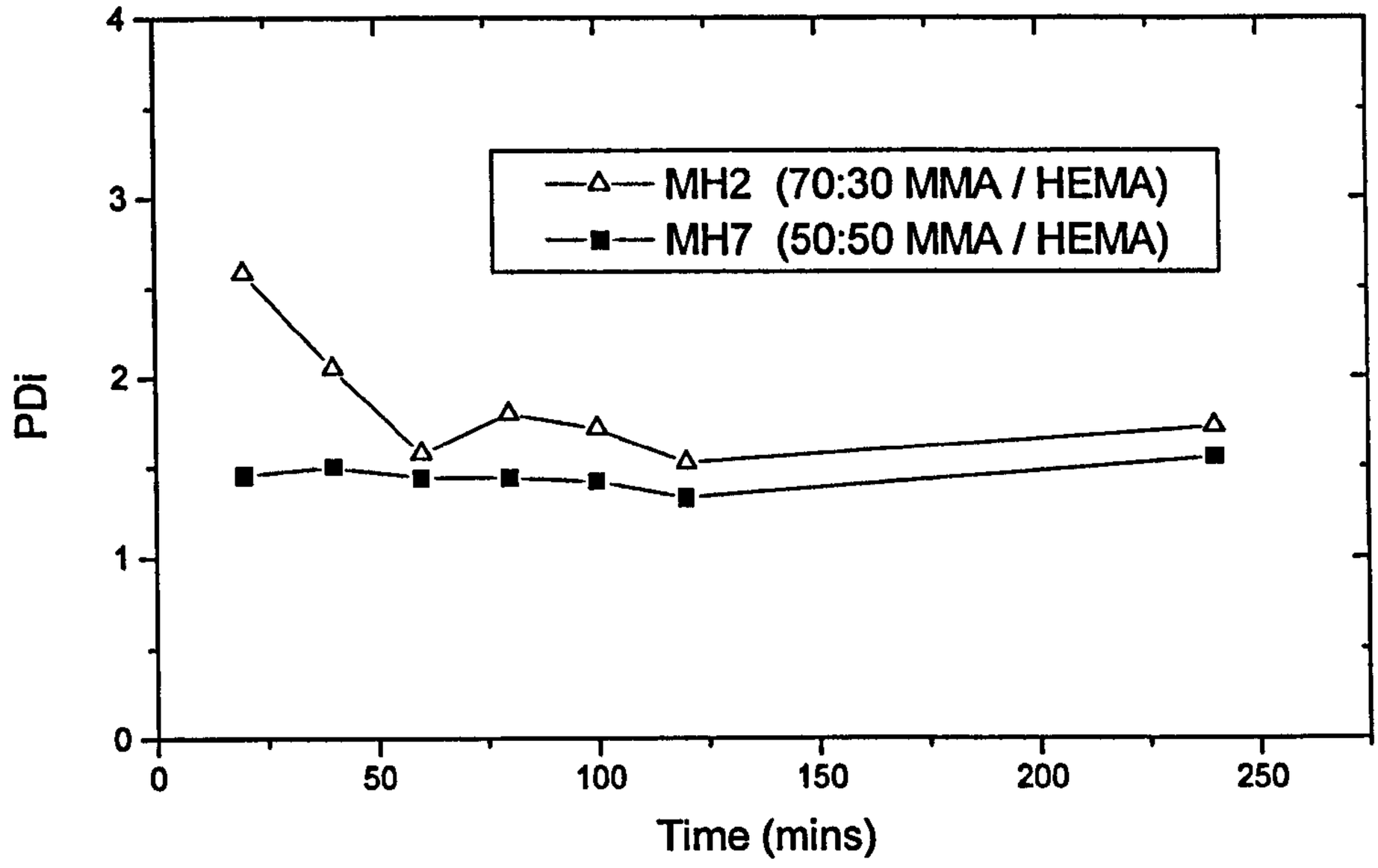

Figure 3.13 – *Polydispersity index versus time graph for emulsion polymerisations MH2 and MH7*

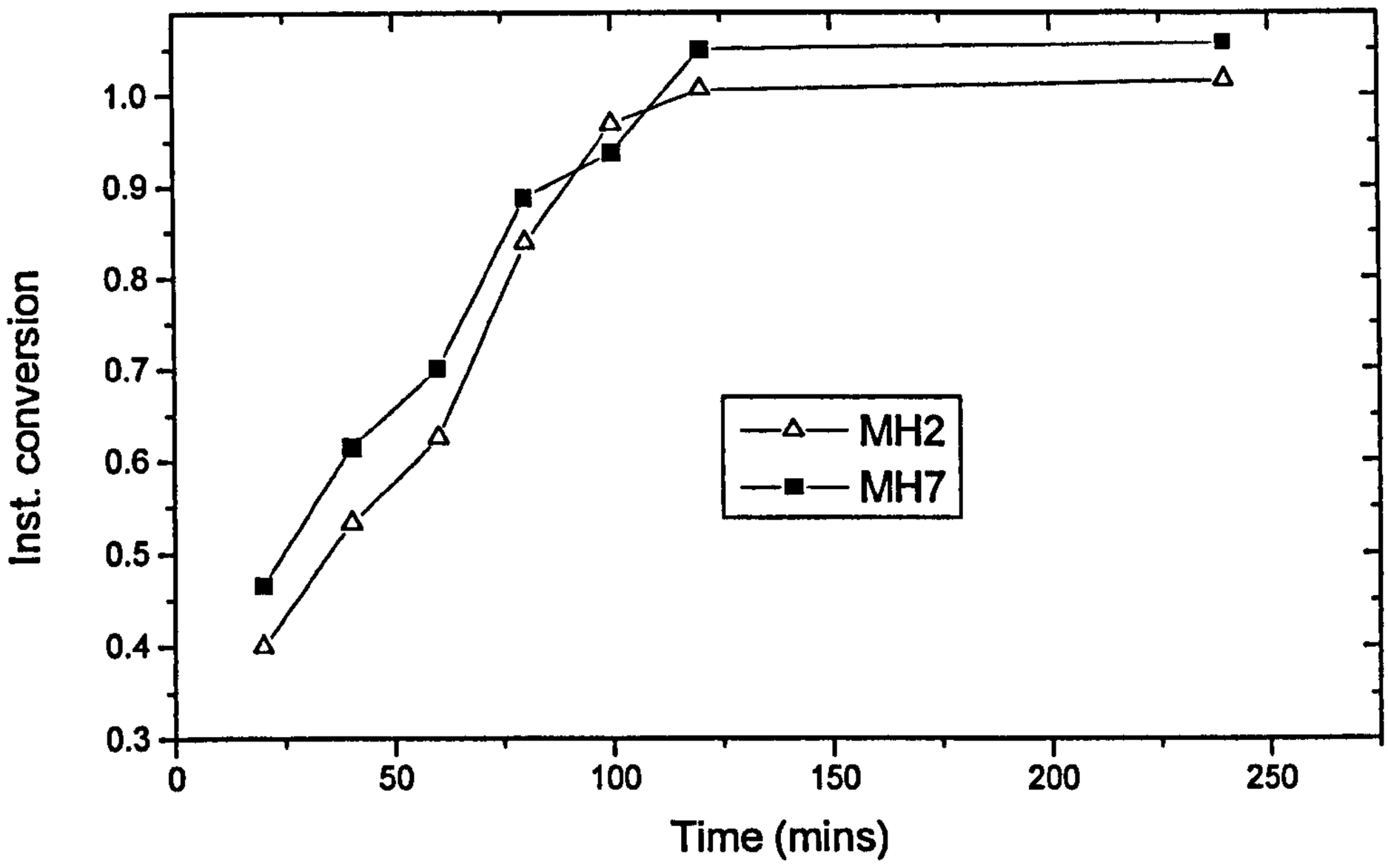

Figure 3.14 – *Instantaneous conversion versus time graph for emulsion polymerisations MH2 and MH7*

It can be seen that the CCT reaction is not affected much by the addition of greater amounts of HEMA into the polymeriation system. The rate of polymerisation (as shown by the instantaneous conversion vs time graph) is also very similar to that for the lower amount of HEMA.

3.3 The CCT Emulsion Polymerisation of MMA/Butyl Acrylate

Co-polymers of methacrylates and acrylates are often used in products for which a low glass transition temperature is required such as for coatings applications. Work was carried out to see if it is possible to synthesise macromonomers comprising of a mixture of methyl methacrylate and butyl acrylate monomer units. Butyl acrylate itself does not possess a terminal methyl group and so is not susceptible to catalytic chain transfer with COBF but instead undergoes living polymerisation with cobalt complexes[6]. Any macromonomers formed by a performing the CCT polymerisation on a mixture of MMA/BA will therefore have to be terminated with a methyl methacrylate group if effective CCT is to be observed. It has been shown that pseudo-living type polymerisation of acrylates may be performed by the use of cobalt porphyrin complexes[Wayland][7] (see figure 3.15). A reversible cobalt - acrylate bond is formed which prevents termination of the propagating chain. For the system to be effective, i.e. little termination, the equilibrium must lie to the right in figure 3.15.

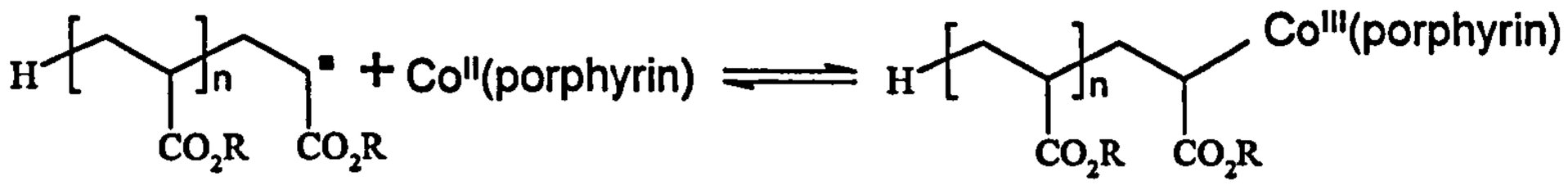

Figure 3.15 – *Pseudo living polymerisation of acrylates using a cobalt porphyrin complex.*

The reaction shown in figure 3.15 means that the effective concentration of CCT agent in the methacrylate/acrylate co-polymerisation could be reduced by some of the catalyst being trapped with the acrylate and not being able to undergo the catalytic chain transfer reaction.

The target polymer in the next set of reactions is illustrated in figure 3.16.

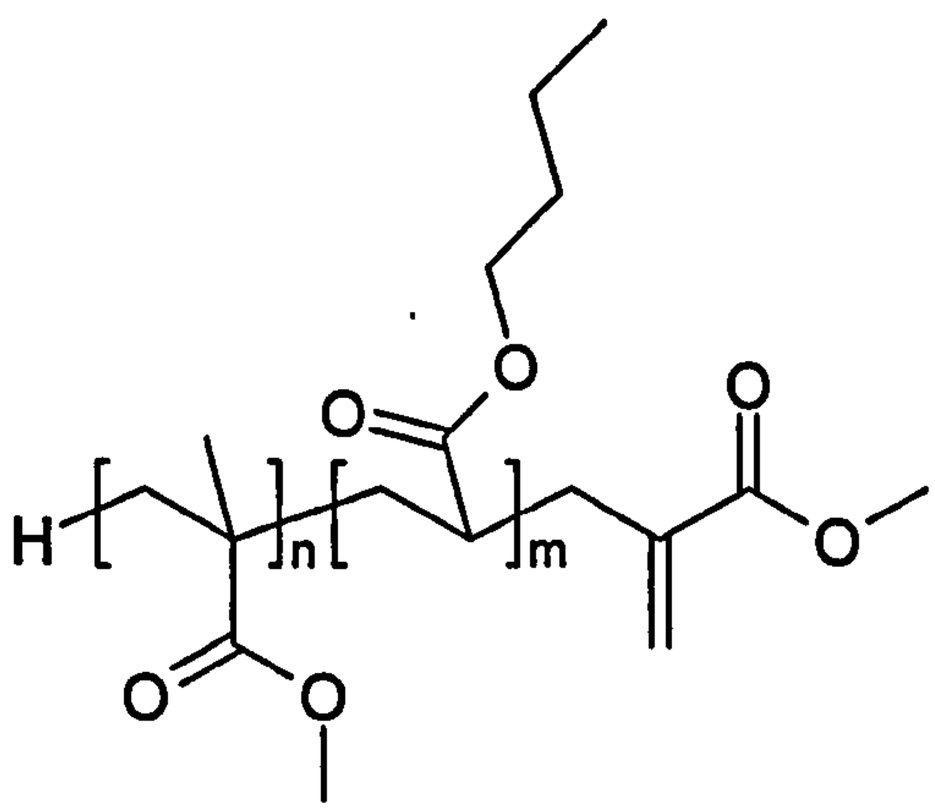

Figure 3.16 – *Structure of MMA/Butyl Acrylate statistical macromonomer*

3.3.1 MMA/BA (50:50) molar ratio

In this section MMA/Butyl acrylate CCT emulsion polymerisations were carried out in order to see if the synthesis of macromonomers with a 50:50 ratio of the

monomers could be accomplished. The end properties of these polymerisations are shown in table 3.5.

Reaction	Wt. COBF (g)	Ppm COBF	Feed Conditions	M_n	PDi	Inst. Conv.	Cs^E
MA1	0.0402	56.10	100% fed	56000	2.52	0.920	36
MA2	0.0291	40.60	100% fed	51100	2.48	0.980	24
MA3	0.0230	35.86	100% fed	73500	2.06	0.990	43
MA4	0.0150	20.93	100% fed	89600	3.10	0.988	61
MA5	0.0000	0.00	100% fed	420000	2.54	0.957	-

Table 3.5 – *End properties for emulsion polymerisations MA1-MA5*

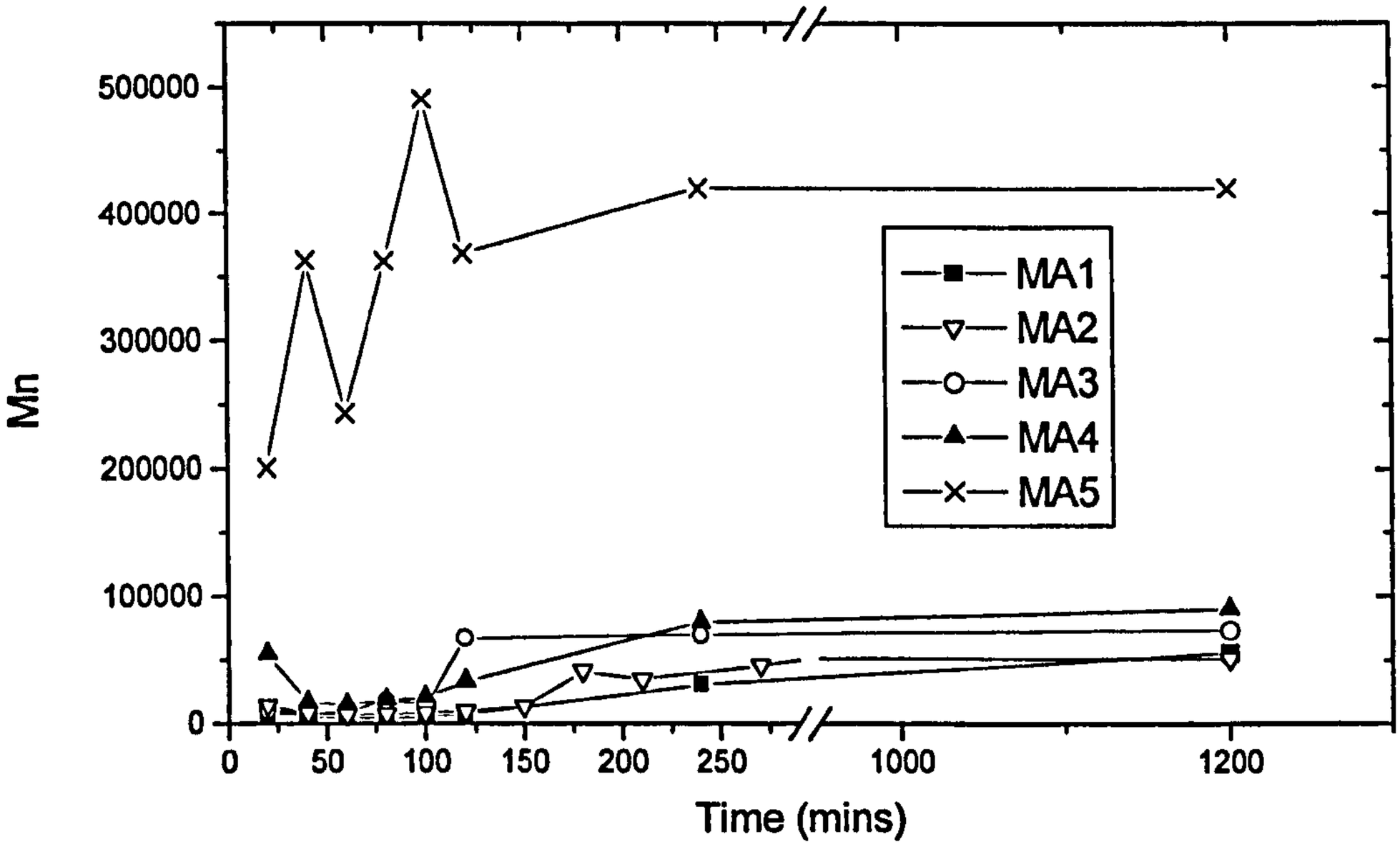

Figure 3.17 – *M_n versus time graph for emulsion polymerisations MA1-MA5*

The plot of the molecular weight of the formed MMA/BA polymers versus time is shown in figure 3.17. It can be seen that the molecular weight of the co-polymers has been greatly reduced on the addition of COBF catalytic chain transfer agent to the system. Figure 3.18 shows a plot of just the reactions with CCT agent allowing the change in molecular weight with time to be seen more clearly.

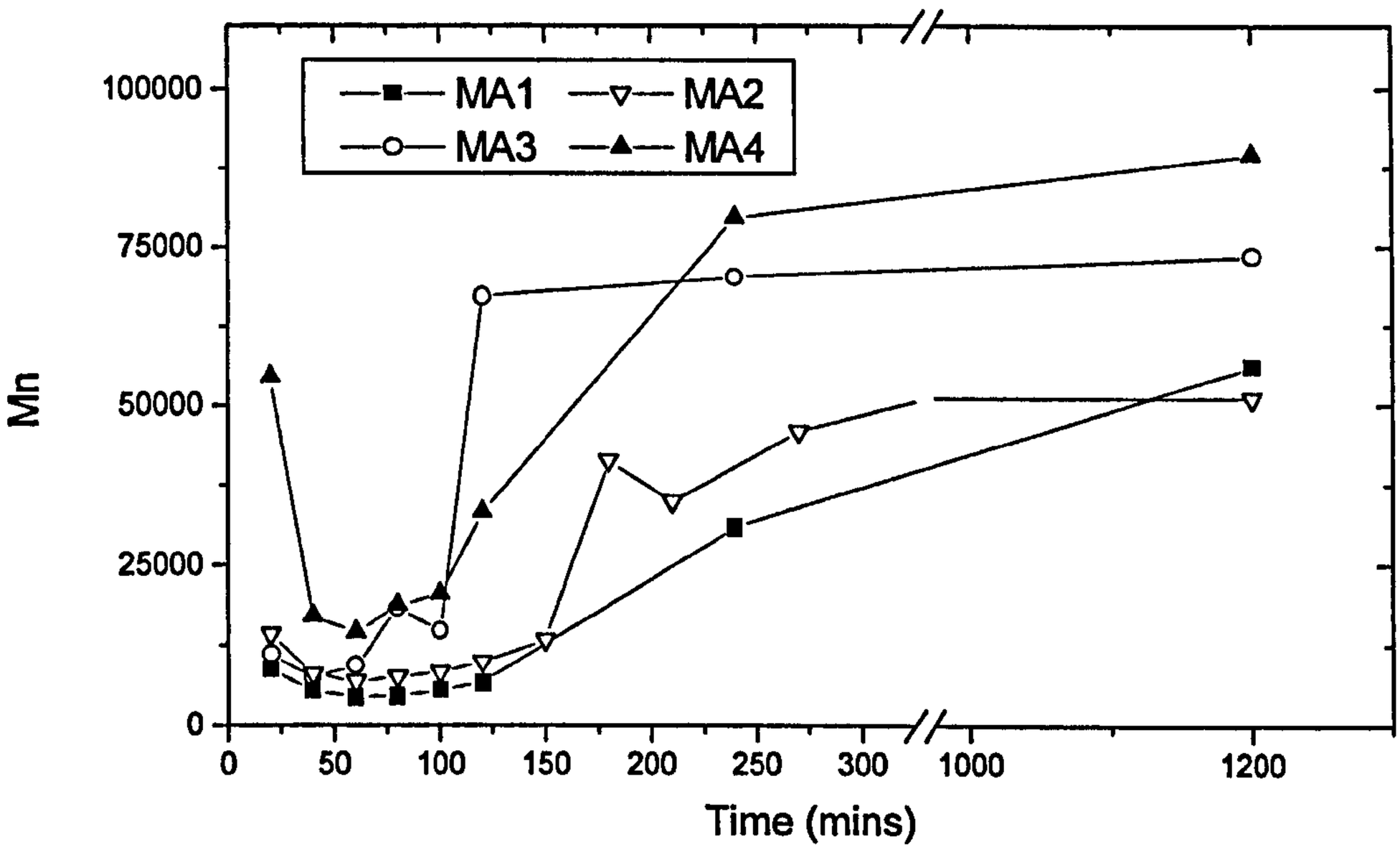

Figure 3.18 – *M_n versus time graph for emulsion polymerisations MA1-MA4*

The graph shown in figure 3.18 shows the large change in molecular weight that is observed through the reaction. The molecular weight of the polymer formed in the first hour of the reaction decreases with time. The fall in molecular weight is due to the fact that the catalyst/monomer mixture is fed into a fixed amount of aqueous phase and hence there will be an increase in the concentration of the COBF catalyst in the particles during this time. The molecular weight of the polymer is fairly low at the early stages of the reaction with molecular weights

that would be expected for typical CCT reactions in emulsion. After the first two hours the molecular weight rises sharply giving an end product with high molecular weight.

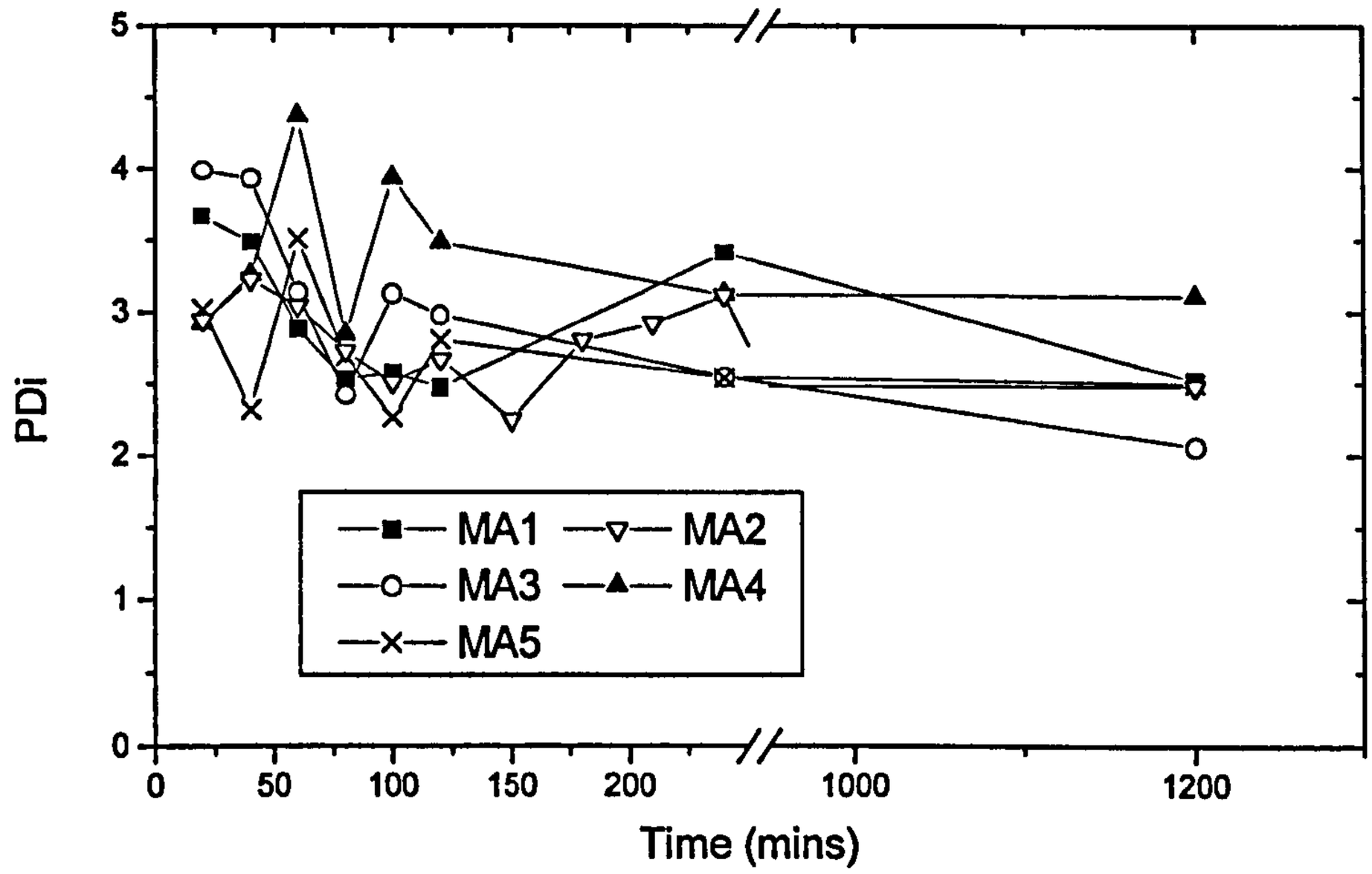

Figure 3.19 – *Polydispersity index versus time graph for emuslion polymerisations MA1-MA5*

The polydispersity index of the products formed from these reactions is shown in figure 3.19. It appears that the polydispersity index is slighty higher than for the equivalent pure MMA polymerisations (section 2.2).

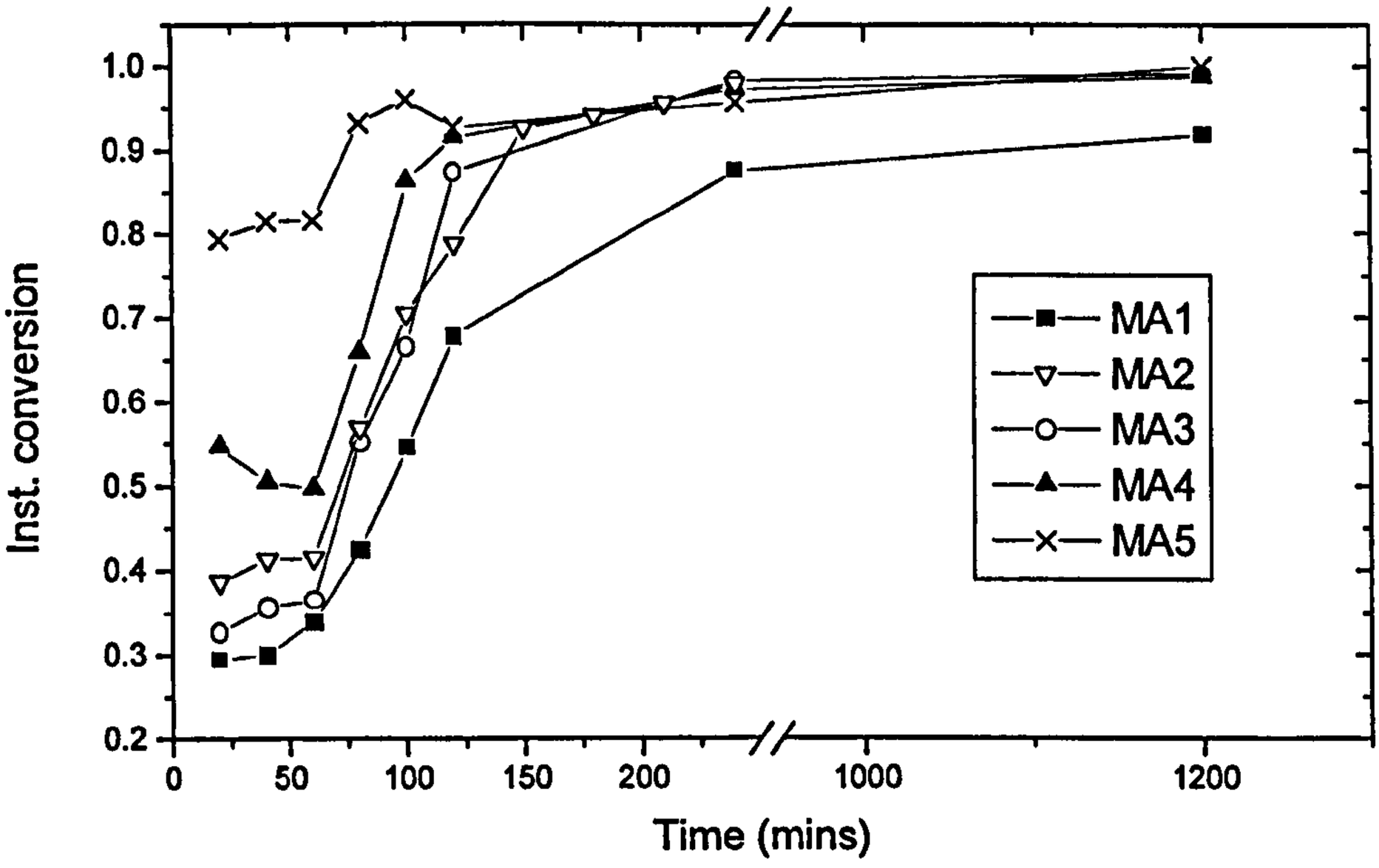

Figure 3.20 – *Instantaneous conversion versus time graph for emulsion polymerisations MA1-MA5*

The rate of polymerisation is shown in figure 3.20. The instantaneous conversion plots for each polymerisation again appears to be quite similar in appearance to the pure MMA emulsion polymerisations with the rates being only slightly slower for the MMA/BA polymerisations.

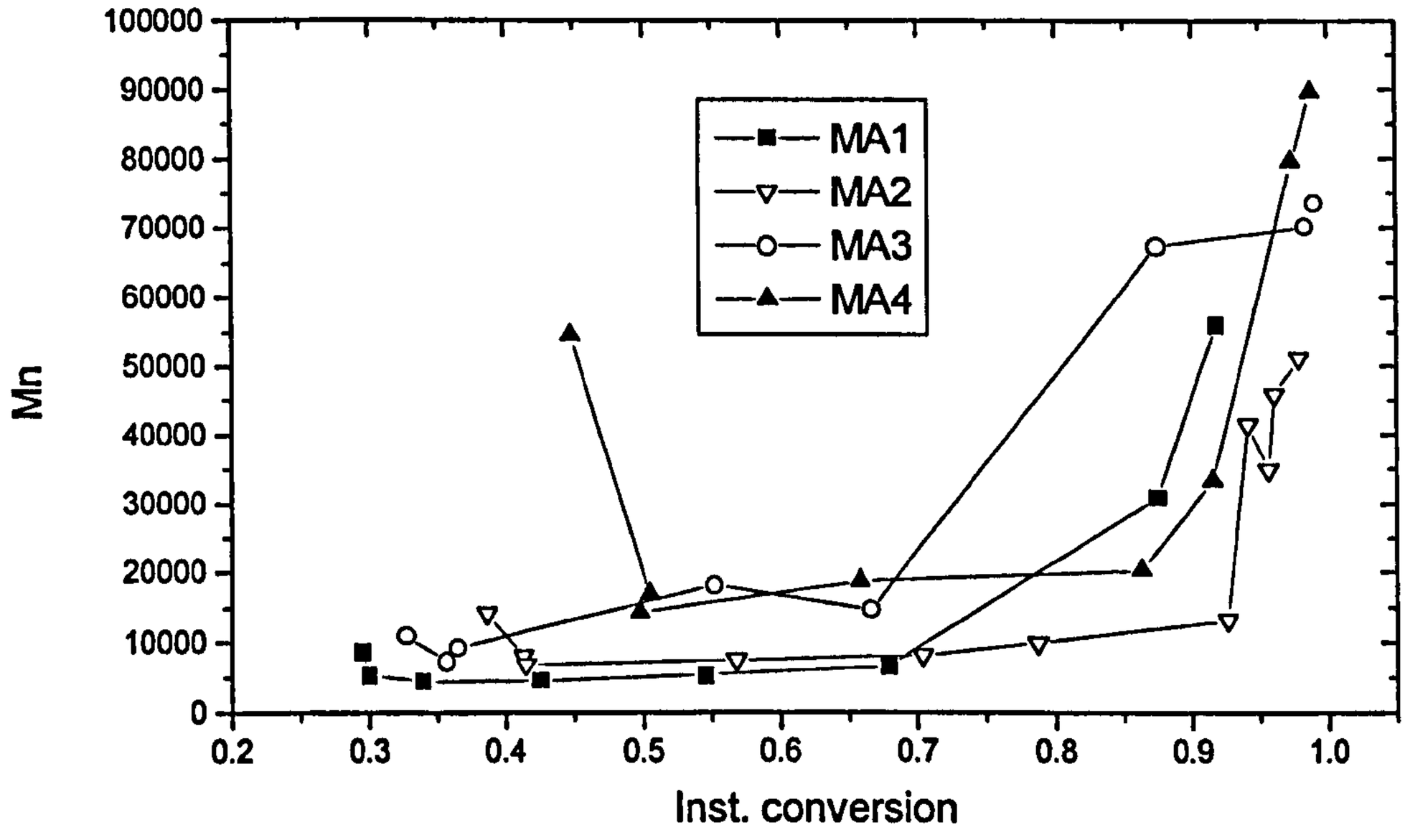

Figure 3.21 – *Instantaneous conversion versus M_n graph for emulsion polymerisations MA1-MA4*

By looking at the M_n versus instantaneous conversion plot is possible to determine that the rise in molecular weight occurs after the polymerisation has reached at least ~70% conversion (i.e. 70% of the monomer has been converted to polymer). The rapid rise in molecular weight could be due to two possible reasons.

1) Compositional drift will occur as the polymerisation proceeds.

The reactivity ratios of the two monomers are given as $r_{MMA} = 2.279$ and $r_{BA} = 0.395$ [8]. Using the terminal model of co-polymerisation it is possible to write equations (3.1) – (3.4).

$$\sim\sim\sim\sim MMA^{\bullet} + MMA \xrightarrow{k_{11}} \sim\sim\sim\sim MMA - MMA^{\bullet} \qquad (3.1)$$

$$\sim\sim\sim\sim MMA^{\bullet} + BA \xrightarrow{k_{12}} \sim\sim\sim\sim MMA - BA^{\bullet} \qquad (3.2)$$

$$\sim\sim\sim\sim BA^{\bullet} + MMA \xrightarrow{k_{21}} \sim\sim\sim\sim BA - MMA^{\bullet} \qquad (3.3)$$

$$\sim\sim\sim\sim BA^{\bullet} + BA \xrightarrow{k_{22}} \sim\sim\sim\sim BA - BA^{\bullet} \qquad (3.4)$$

Where: $r_{MMA} = \frac{k_{11}}{k_{12}} = 2.279$ $\qquad$ $r_{BA} = \frac{k_{22}}{k_{21}} = 0.395$

The reactivity ratios indicate that reaction (3.1) is faster than reaction (3.2) and also reaction (3.3) is faster than reaction (3.4). This will mean that methyl methacrylate will be consumed much faster in the polymerisation than the butyl acrylate.

At the end of the polymerisation there will be an excess of butyl acrylate, which cannot undergo chain transfer with the COBF catalyst, so the molecular weight of the polymer would be expected to rise rapidly. If the reactivity ratios for MMA and BA are inserted into the co-polymer equation it is possible to plot the composition of the co-polymer made from the two monomers as a function of the feed composition (figure 3.22.)

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \qquad (3.5)\ \textit{Co-polymer equation}$$

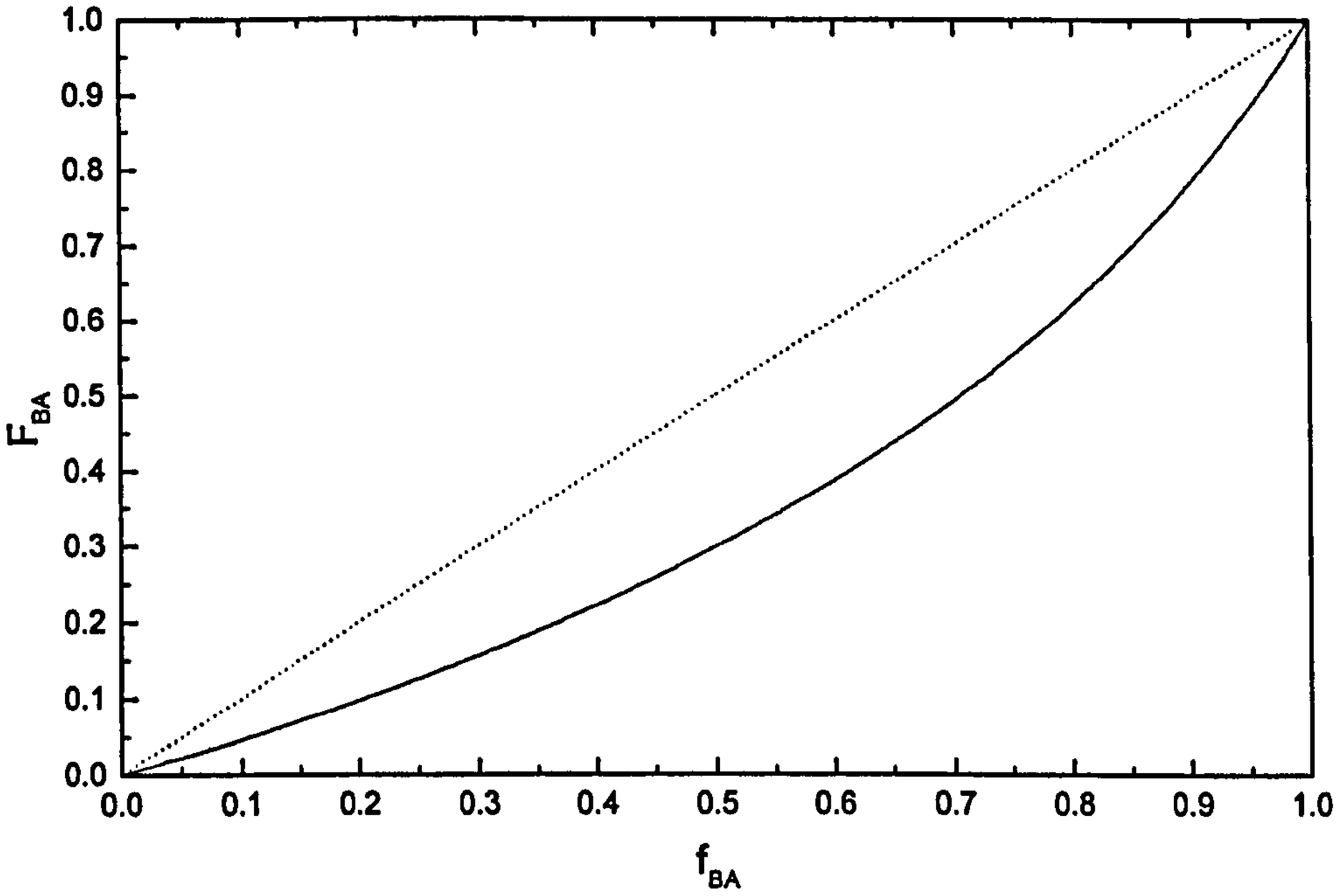

Figure 3.22 – *Plot of composition of MMA/BA co-polymer as a function of feed composition using $r_{MMA} = 2.279$ and $r_{BA} = 0.395$*

The graph shown in figure 3.22 predicts that there will be a noticeable deviation of the co-polymer composition from the composition in the feed. The graph shown in figure 3.22 is really only useful at low conversions (under 5%) since above that conversion there will be a noticeable change in the monomer feed composition as the reaction proceeds (i.e. f_{BA} will not remain constant). At low conversion for a 50:50 ratio of monomers, as polymerised in the experiments in this section, there is predicted to be only 30 % butyl acrylate in the polymer.

2) The increase in molecular weight of the polymers could also be due to butyl acrylate ended propagating polymer radicals reacting with macromonomers

formed in the early stages of the reaction which would lead to the formation of graft polymers.

The fact that the molecular weight of the polymerisations is low through the early stages of the reaction suggests that the reaction of a butyl acrylate ended polymer radical with an MMA monomer unit and the subsequent termination by a chain transfer event is much favoured over the grafting reaction. At the later stages of the reaction, where there is less MMA present compared to butyl acrylate, the grafting may occur to a significant extent.

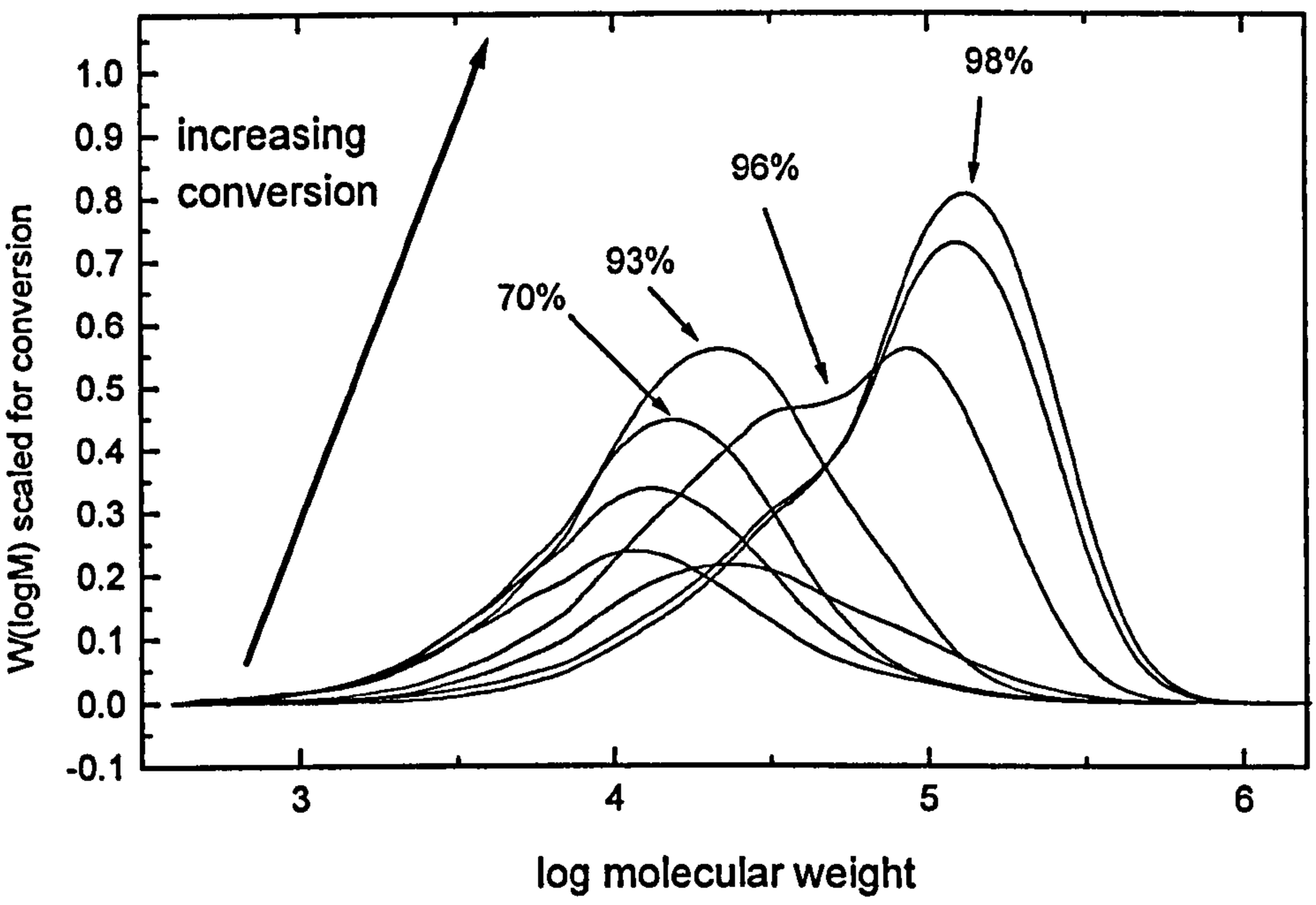

Figure 3.23 – *SEC chromatograms from experiment MA2*

If the SEC chromatograms for reaction MA2 are plotted (figure 3.23) the change in molecular weight at the latter stages of the reaction is evident. It can be seen that the increase in molecular weight is only observed at high conversions greater

than 90 %. At 93% conversion (M_n = 13200) the SEC trace is similar to the chromatograms earlier in the reaction, implying that effective macromonomer synthesis is still occurring. At 96% conversion (M_n = 45800) there is a large increase in molecular weight, although there is only a small increase in conversion (3%), which suggests that the macromonomer is forming graft co-polymers with the remaining butyl acrylate monomer left in the system.

If the instantaneous co-polymer equation is used, equation (3.6), then it is possible to predict the composition of the feed and the resulting polymer through the reaction.

$$1-\frac{M}{M_0}=1-\left[\frac{f_1}{(f_1)_0}\right]^{\alpha}\left[\frac{f_2}{(f_2)_0}\right]^{\beta}\left[\frac{(f_1)_0-\delta}{f_1-\delta}\right]^{\gamma}$$

(3.6) *Instantaneous co- polymer composition equation*

where :

$$\alpha=\frac{r_2}{(1-r_2)} \qquad \beta=\frac{r_1}{(1-r_1)}$$

$$\gamma=\frac{(1-r_1r_2)}{(1-r_1)(1-r_2)} \qquad \delta=\frac{(1-r_2)}{(2-r_1-r_2)}$$

Equation 3.6 allows us to calculate the variation with conversion of the fraction of each monomer in the feed and the monomer ratios in the polymer being synthesised at a given moment in the polymerisation. Also it is possible to calculate the overall average composition of the polymer in the reaction vessel as a function of conversion.

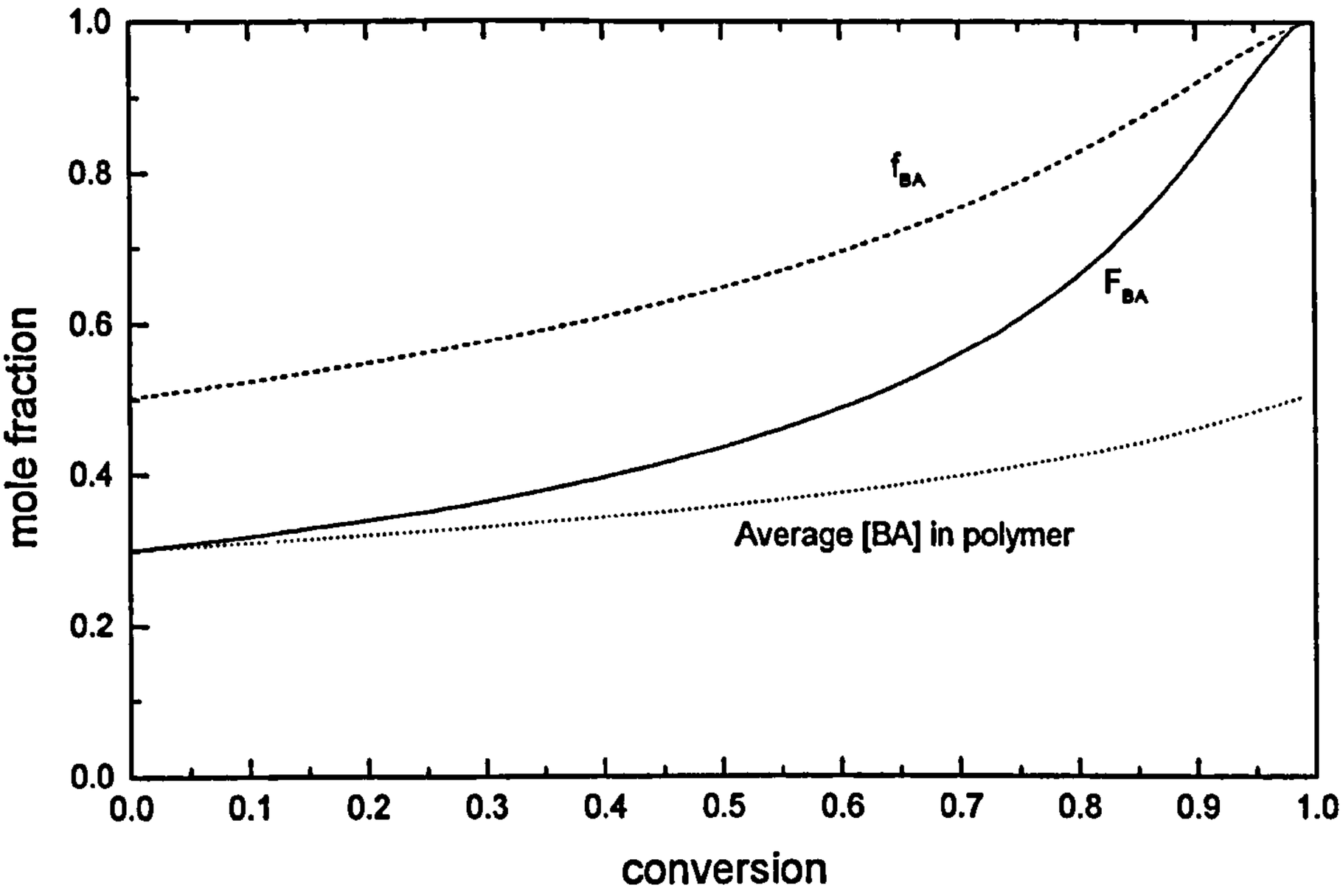

Figure 3.24 - *Calculated Instantaneous Co-polymer Composition for MMA/BA co-polymers (50:50 ratio of monomers)*

At 96% conversion it is predicted that the remaining monomer is composed of 98% butyl acrylate and only 2% methyl methacrylate and so it is likely that the remaining propagating butyl acrylate polymer chains, which are unable to terminate by catalytic chain transfer, will encounter macromonomer chains and react to form graft co-polymers. This supposition is supported by the fact that the SEC chromatograms shown in figure 3.23 are scaled for conversion, this means that if the macromonomer formed early in the reaction were not reacting to form graft co-polymers then the high molecular weight peak for the 96% conversion sample should only be 3% the size of the low molecular weight peak, which is clearly not the case.

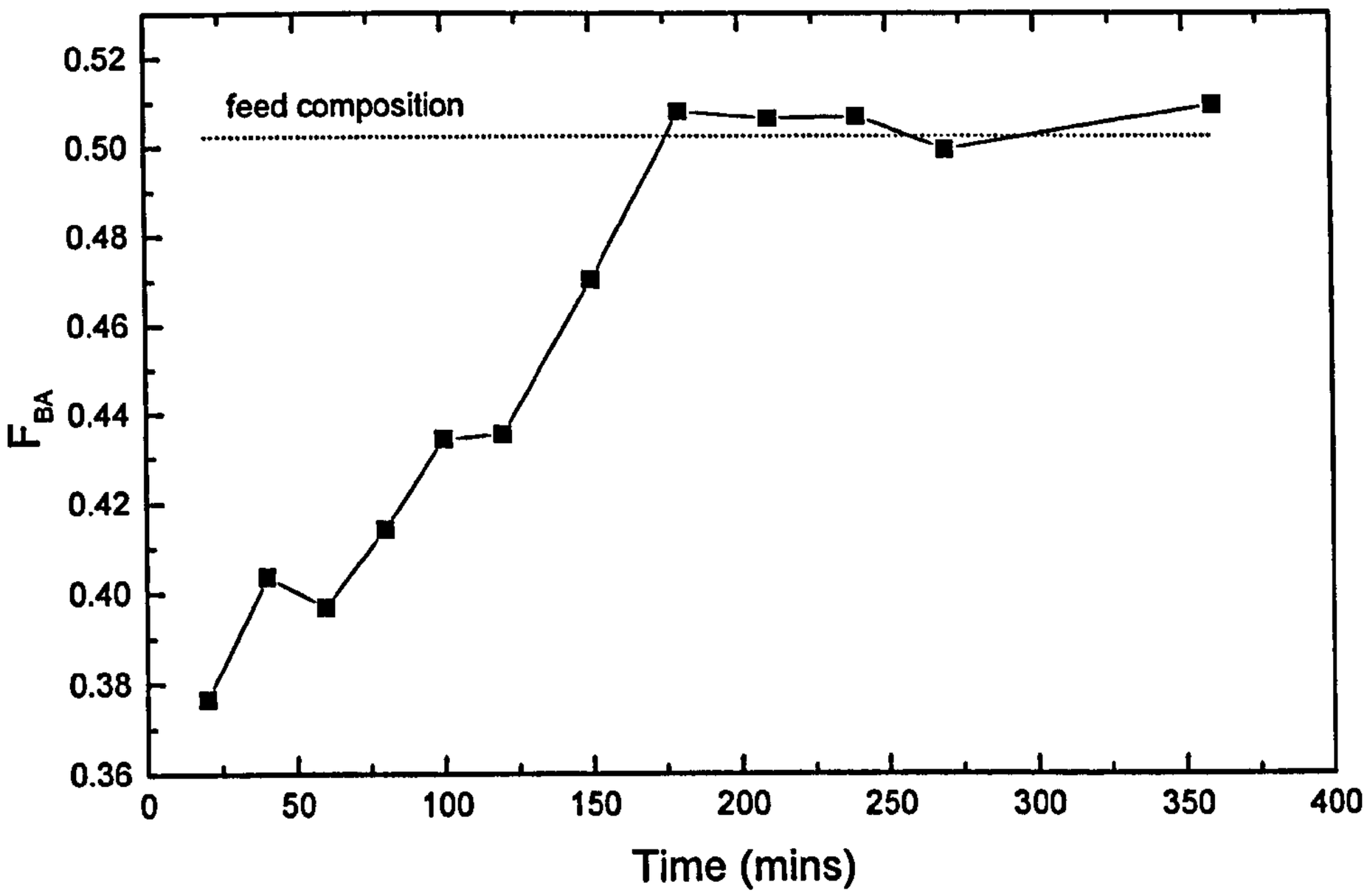

Figure 3.25 – *Fraction of butyl acrylate in the polymer synthesised in reaction MA2 versus time as measured by NMR.*

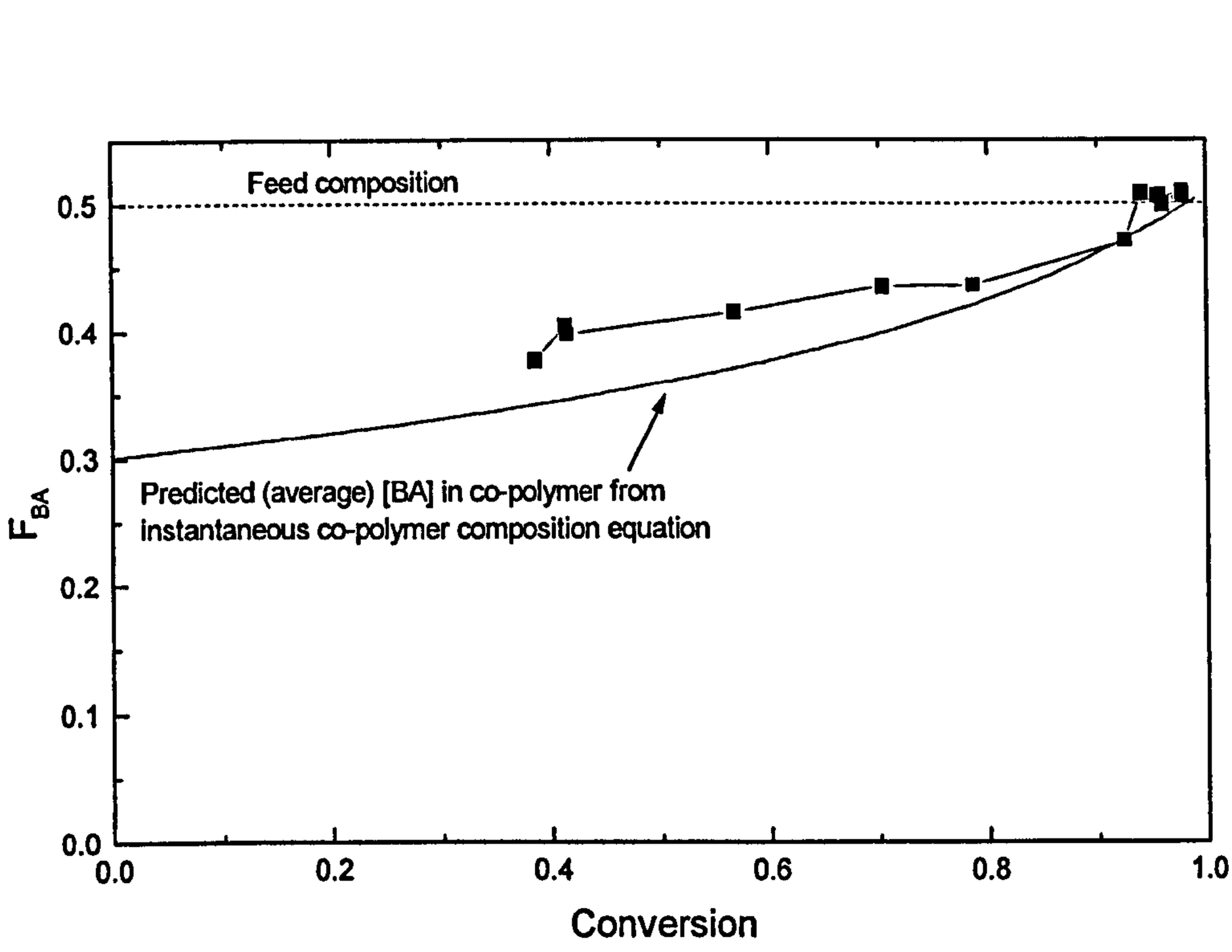

Figure 3.26 – *Fraction of BA in the polymer synthesised in reaction MA2 as a function of conversion, measured by NMR.*

The NMR data for experiment MA2 is shown in figure 3.25. The change in composition of the polymer through the course of the reaction is shown.

In figure 3.26 the amount of butyl acrylate in the polymer is shown in relation to the instantaneous conversion of the reaction. It can be seen that the amount of BA in the polymer as measured by NMR deviates slightly from that predicted by the instantaneous composition equation. The polymer appears to be richer in butyl acrylate than expected, this could be due to the fact that butyl acrylate has a lower water solubility than the MMA (MMA is water soluble to 15 g/L and BA is soluble to 1.6 g/L [9]) and so the acrylate concentration in the particles will be higher than the MMA concentration resulting in an increased amount of acrylate in the polymer than predicted.

The data in figures 3.25 and 3.26 show the compositional drift through the reaction that was predicted by use of the instantaneous co-polymer composition equation. Using the data obtained from the NMR experiments it is possible to determine the partial monomer conversions for the reaction (i.e. the conversion as calculated separately for each monomer). Again as predicted the methyl methacrylate is consumed quicker than the butyl acrylate and at the later stages of the reaction there is a negligible amount of methacrylate present compared to the acrylate.

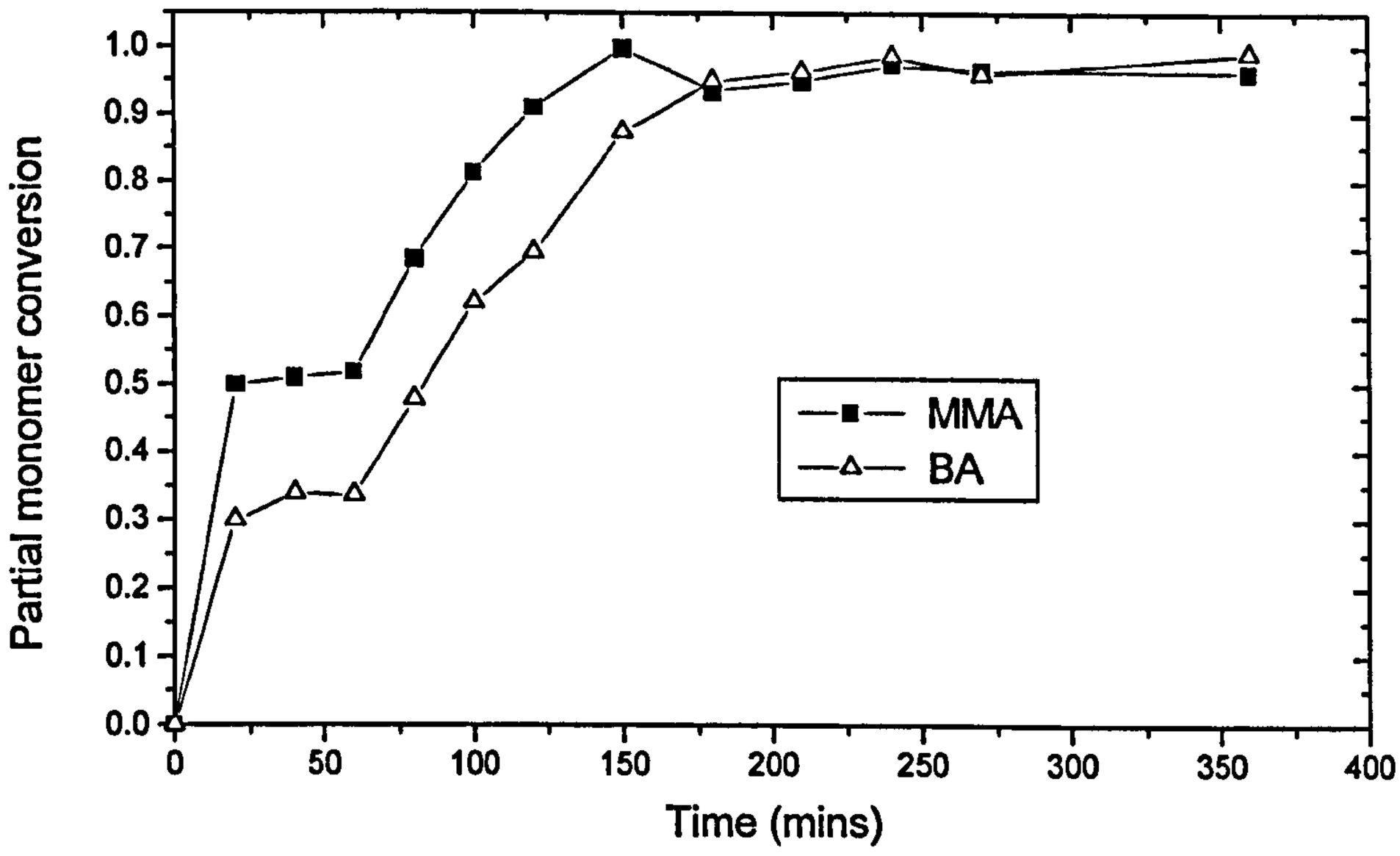

Figure 3.27 – *Partial monomer conversion for experiment MA2*

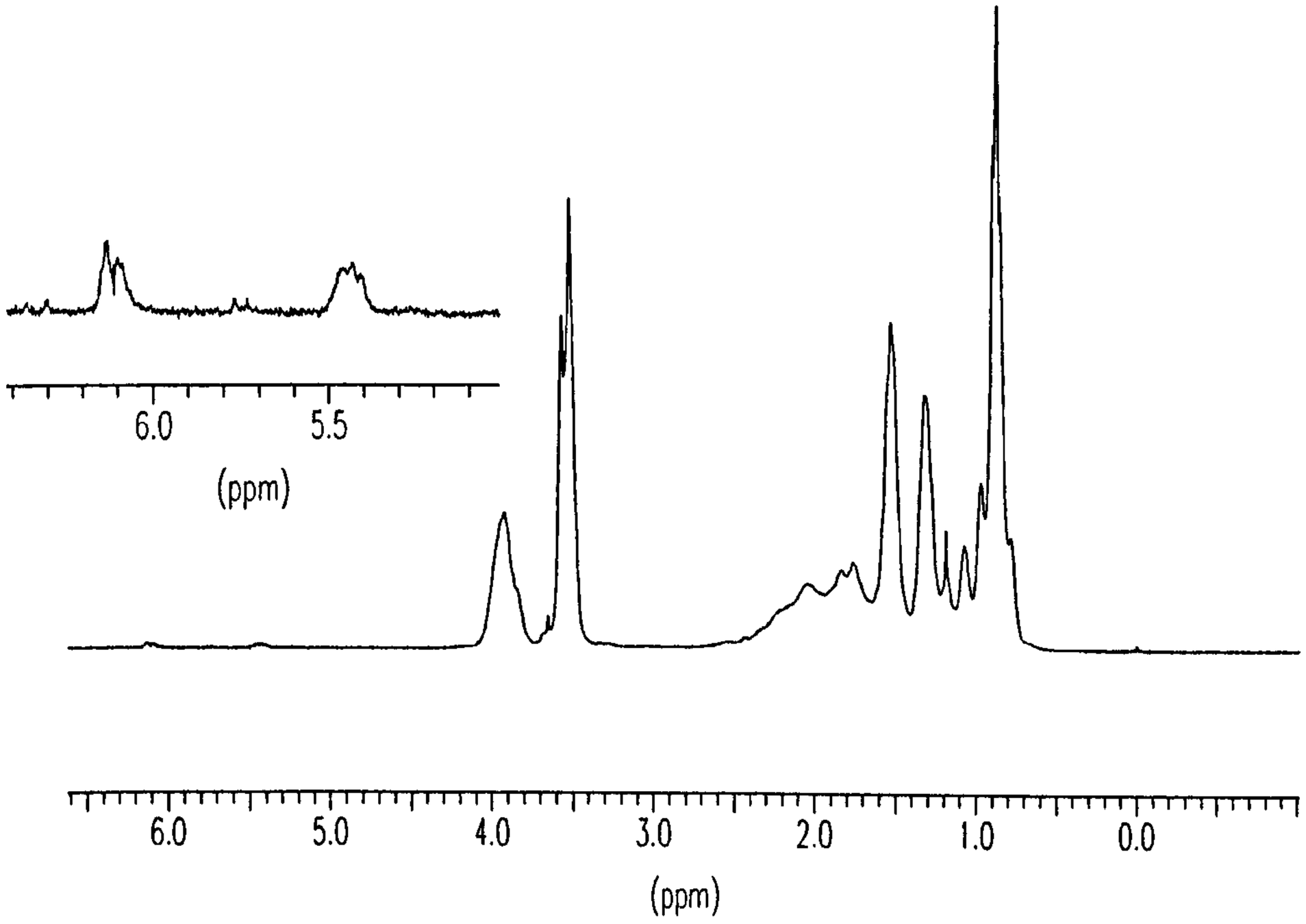

Figure 3.28 – *^{1}H NMR spectrum of MMA/BA statistical co-polymer synthesised in polymerisation MA2 (40 minutes reaction time)*

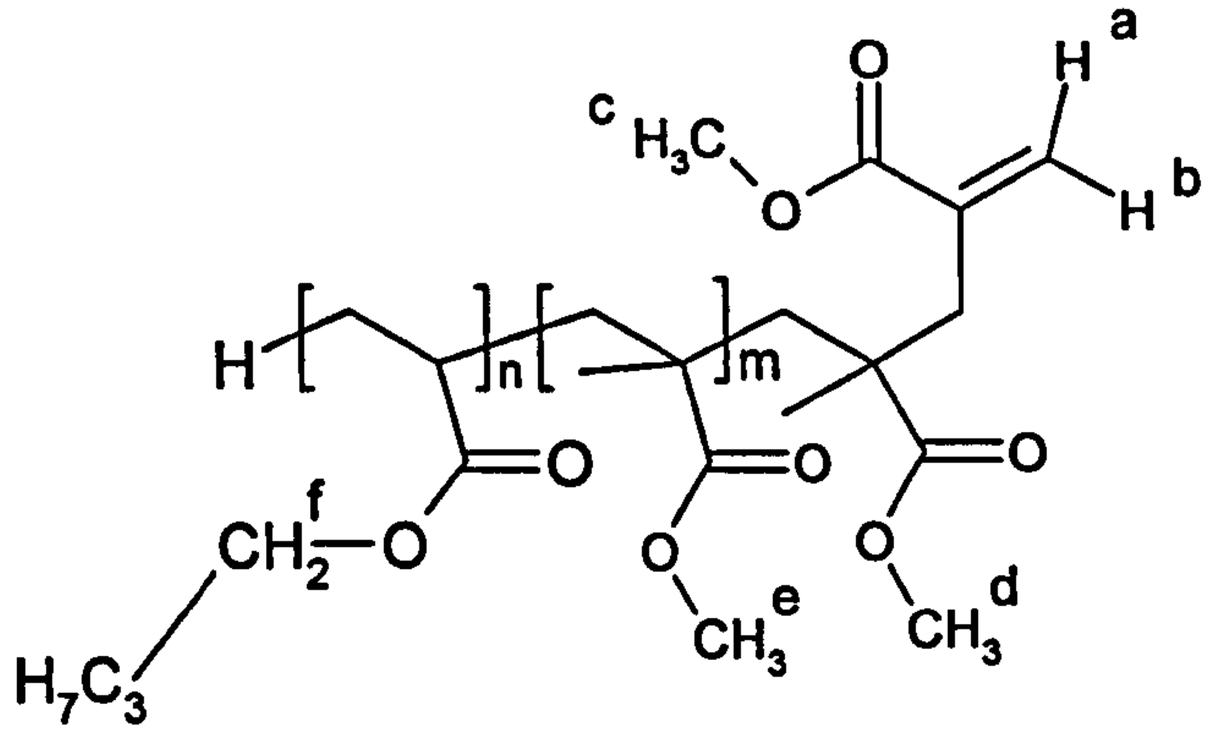

Figure 3.29 – *Structure of MMA/BA statistical co-polymer with protons labelled for NMR analysis*

Peak (ppm)	Integral	Multiplet Type	Assignment
6.15	1.00	singlet	Vinyl proton [a]
5.40	1.02	singlet	Vinyl proton [b]
3.97	52.7	singlet	Proton [f]
3.62	121	singlet	Terminal methoxy proton [c]
3.59		singlet	First in chain methoxy proton [d]
3.57		singlet	Remaining methoxy protons [e]
0.5-3.0	524	multiplets	In chain CH_2 and CH_3 protons

Table 3.6 - *Assignment of peaks for NMR spectrum in figure 3.28*

3.3.1.1 - DSC Analysis of MMA/BA (50:50 molar ratio) co-polymers

Butyl acrylate is often used in co-polymer mixtures to lower the glass transition temperature of a polymer product. The glass transition temperatures for the polymers formed by reactions MA1-MA4 are shown in table 3.7.

Reaction	M_n	M_w	T_g onset / °C	T_g inflection / °C
MA1	56000	141000	-3.2	4.7
MA3	73500	151000	-4.2	4.1
MA4	89600	278000	-7.5	5.4
MA5	420000	1070000	-0.2	7.8

Table 3.7 - *DSC results for MMA/BA statistical co-polymers synthesised in emulsion polymerisations MA1, MA3-MA5*

It can be seen that there is little change in glass transition temperature with the increase in molecular weight. The fact that the T_g does not change significantly with chain length is due to the fact that the samples are sufficiently high molecular weight that the glass transition temperature varies very little with increasing polymer chain size (i.e. the $T_{g\infty}$ value has been reached).

3.2.2 MMA/BA (75:25 molar ratio)

Polymerisations with a lower amount of butyl acrylate were attempted to see if it was possible to prevent the grafting reaction that was observed at high conversions for the 50:50 BA/MMA co-polymerisations. The results are shown in table 3.8.

Reaction	Wt. COBF (g)	Ppm COBF	Feed Conditions	Mn	PDi	Inst. Conv.	Cs^E
MA6	0.0230	32.09	100% fed	10700	1.87	0.997	334
MA7	0.015	20.93	100% fed	13900	2.41	1.010	393
MA8	0.008	11.16	100% fed	26400	2.37	1.021	388
MA9	0.000	0.00	100% fed	177000	3.14	1.041	-

Table 3.8 – *End conditions for MMA/BA emulsion co-polymerisations (75:25 molar ratio of monomers)*

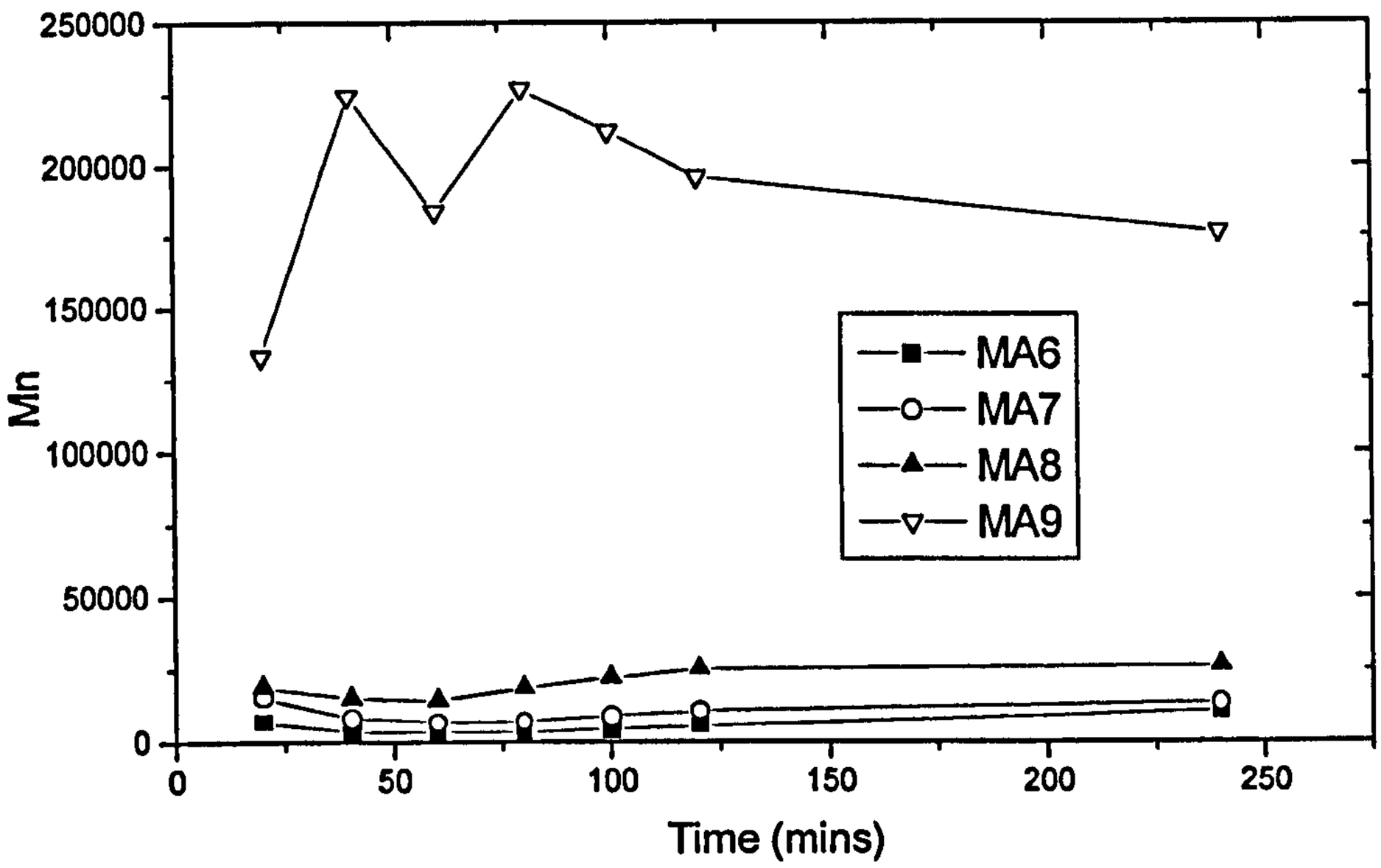

Figure 3.30 – *M_n versus time graph for polymerisations MA6-MA9*

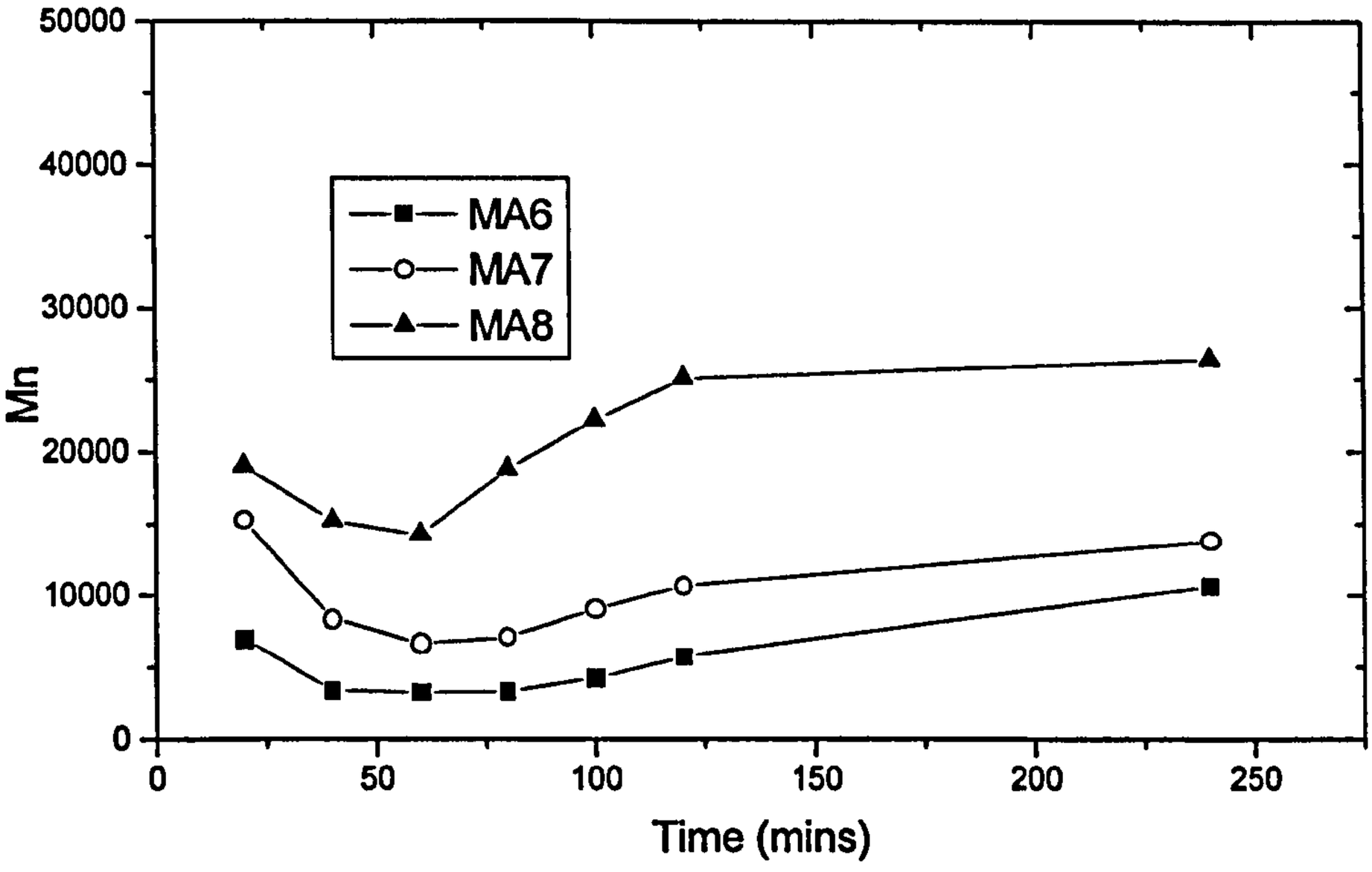

Figure 3.31 – *M_n versus time graph for polymerisations MA6-MA8*

Figure 3.30 shows that the molecular weight of the 75:25 MMA:BA co-polymers has been succesfully reduced on the addition of CCT agent COBF. The increase in molecular weight at the end of the reaction does not appear to be as pronounced as for the 50:50 ratio of monomers. If the M_n versus instantaneous conversion is plotted it is observed that the molecular weight increases late in the polymerisation at high instantaneous conversion.

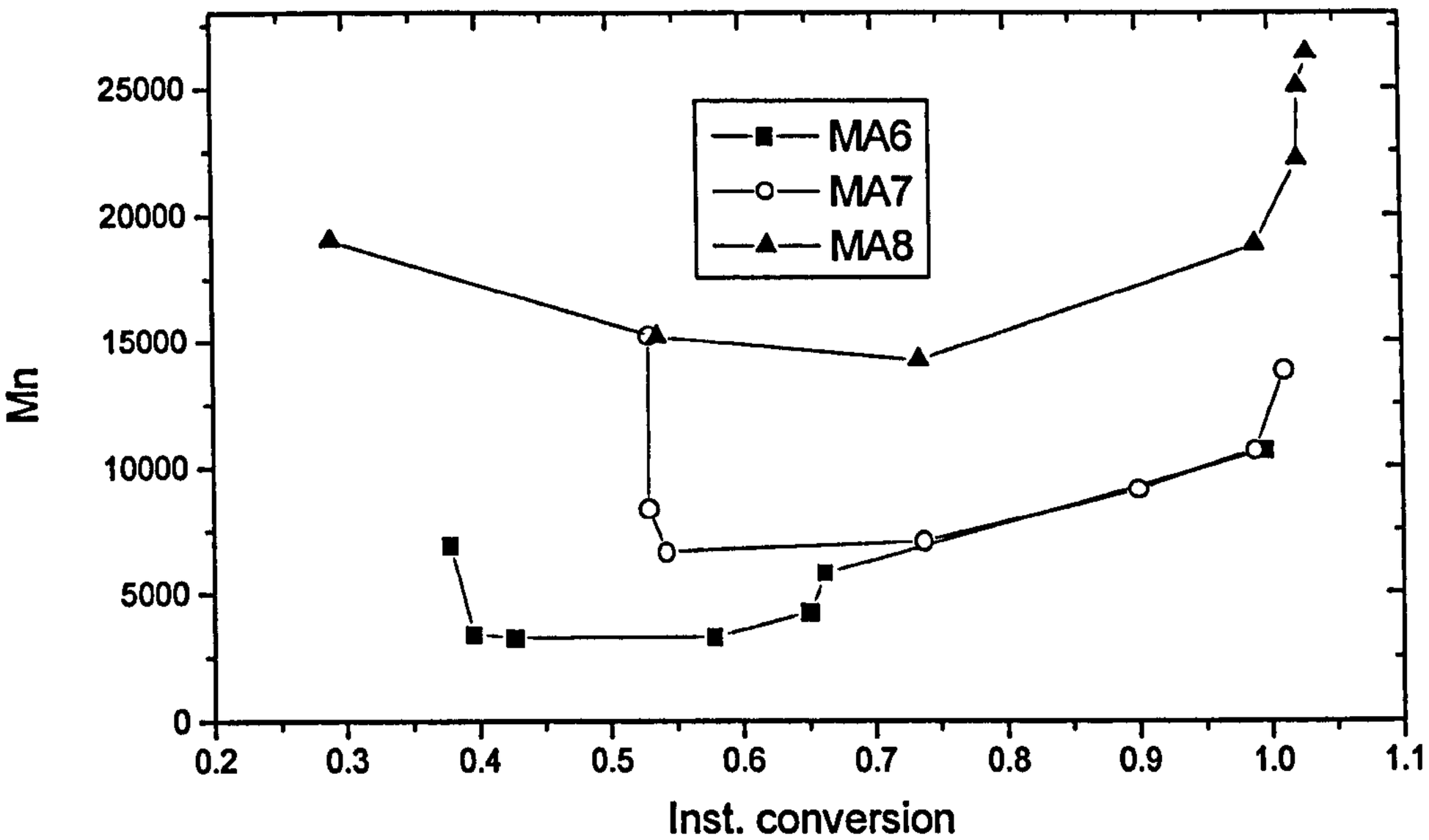

Figure 3.32 – *M_n versus instantaneous conversion graph for reactions MA6-MA8*

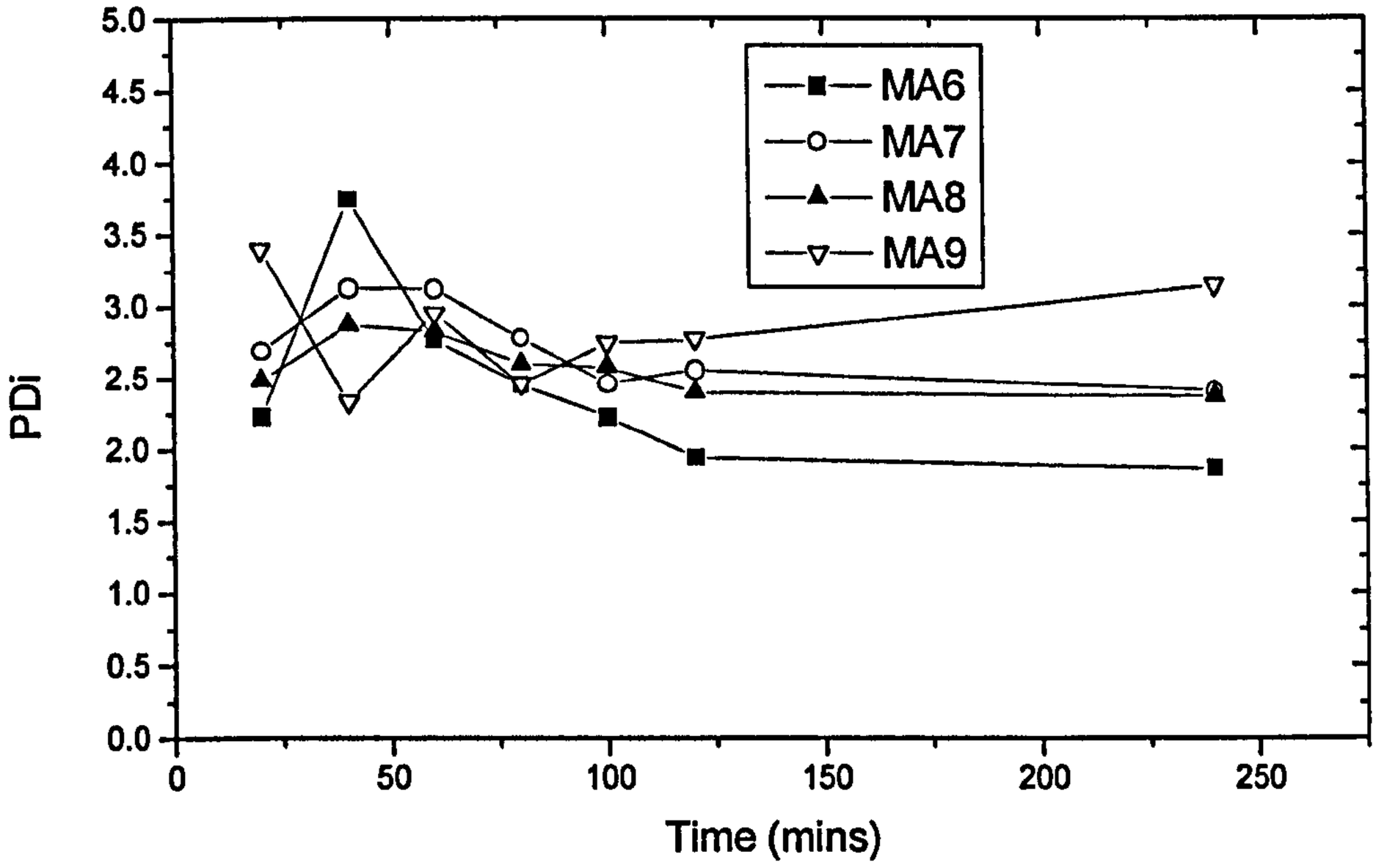

Figure 3.33 – *Polydispersity index versus time graph for emulsion polymerisations MA6-MA9*

The polydispersity indices of the polymers formed in these reactions are reasonably low, as usual for CCT polymerisations.

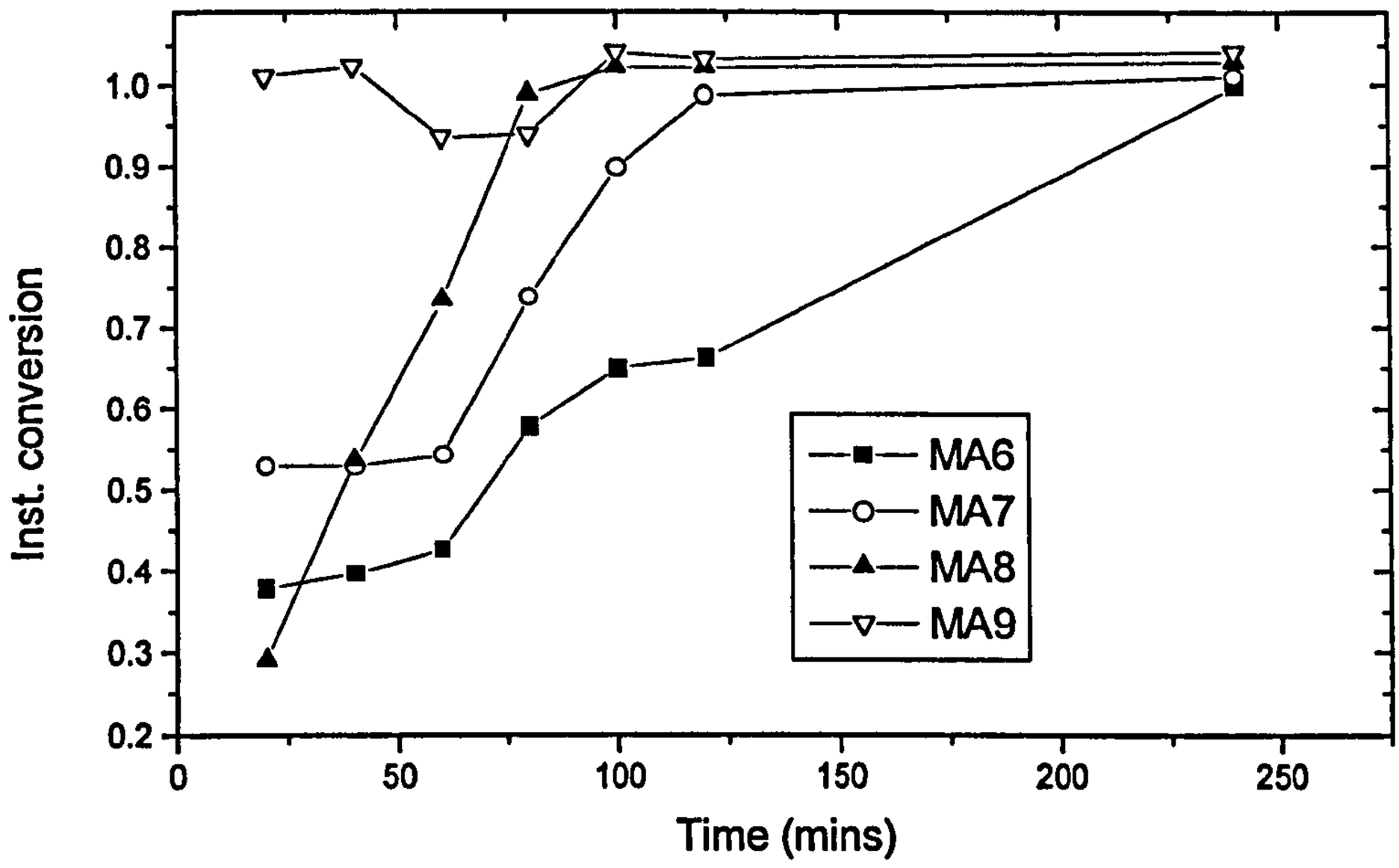

Figure 3.34 – *Instananeous conversion versus time graph for emulsion polymerisations MA6-MA9*

The rates of reaction for these polymerisations are shown in figure 3.34. As shown previously, the addition of CCT agent to a polymerisation slows the rate of reaction and this is demonstrated in figure 3.34 with the more CCT agent being present the slower the rate of reaction. The polymerisations are also slower than the corresponding pure MMA reactions.

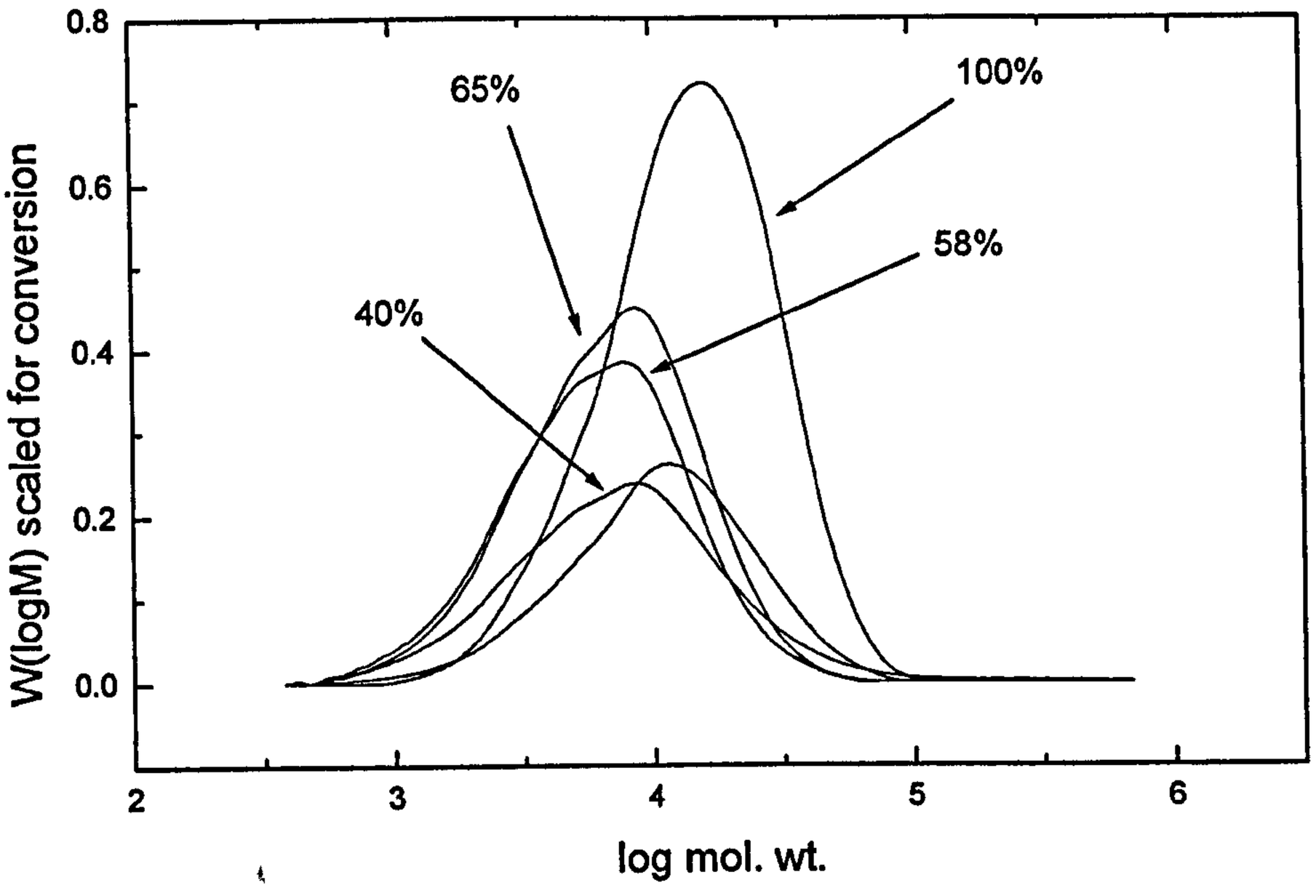

Figure 3.35 - *SEC traces for reaction MA5 (32 ppm COBF)*

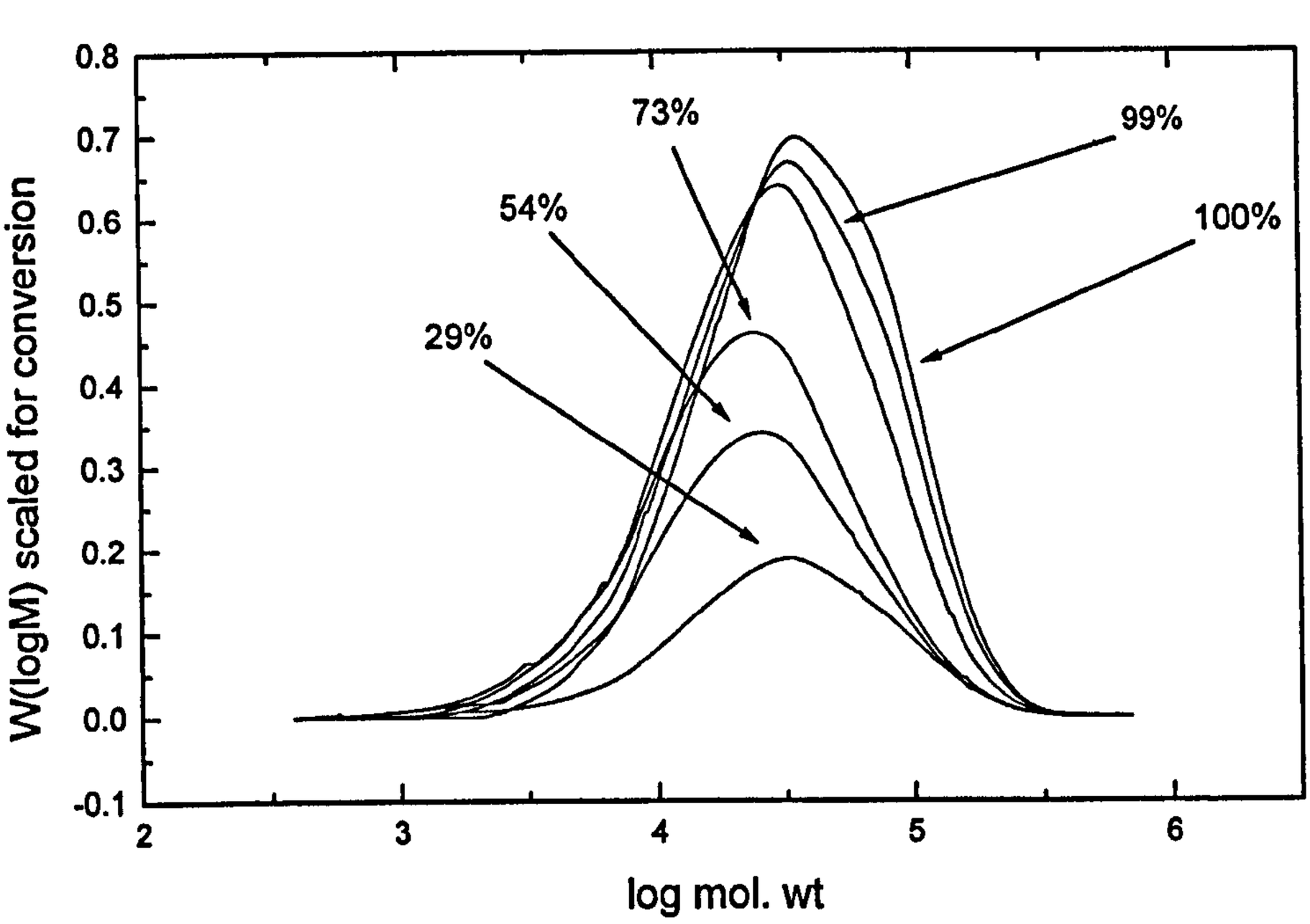

Figure 3.36 - *SEC traces for reaction MA7 (11 ppm COBF)*

If the SEC chromatograms for reactions MA5 and MA7 are drawn and scaled for conversion it is be possible to obtain a greater understanding of the reaction. For reaction MA5 (32 ppm COBF catalyst) it can be seen that as for the 50:50 ratio of monomers there is an increase in molecular weight at high conversion. The increase is not as significant as for the higher amount of acrylate and this would be expected since the methacrylate would not be expected to be consumed until much later in the polymerisation. Using the instantaneous co-polymer composition equation it is possible to predict the amount of the two monomers in the feed and the resulting polymer. The plot for a 75:25 mixture of monomers is shown in figure 3.37.

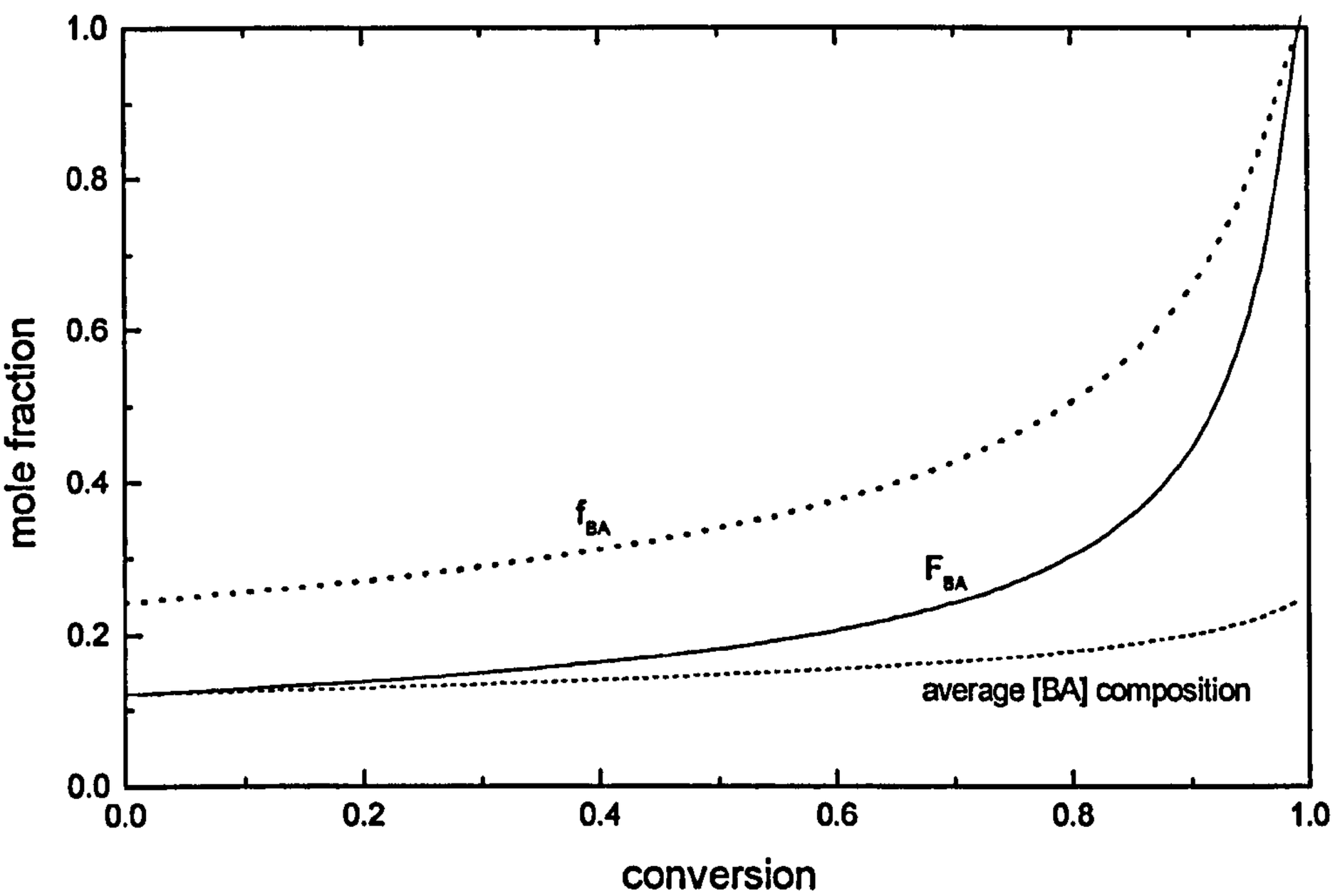

Figure 3.37 - *Calculated Instantaneous Co-polymer Composition for MMA/BA co-polymers (75:25 ratio of monomers)*

At 90% conversion the composition of the remaining monomer is predicted to be still only 44% butyl acrylate and 56% methyl methacrylate. There is therefore still a reasonable concentration of MMA left in the reaction at this stage and so macromonomer synthesis would still be possible at this stage. It is not predicted that until ~98% conversion that there will be a significant decrease in the methyl methacrylate concentration where the ratio of the monomers is calculated as 85% butyl acrylate and 15% MMA. For reaction MA7, which has a lower amount of chain transfer agent (11 ppm), there will be a notable decrease in the concentration of macromonomer vinyl groups (since the molecular weight is higher there will be more repeat units per chain and hence more repeat units per vinyl endgroup) this will mean that the ratio of butyl acrylate: macromonomer vinyl groups will be significantly reduced compared to MA5 and so the amount of grafting would be expected to be reduced. This is observed in the overlayed SEC traces for reaction MA7 (figure 3.36).

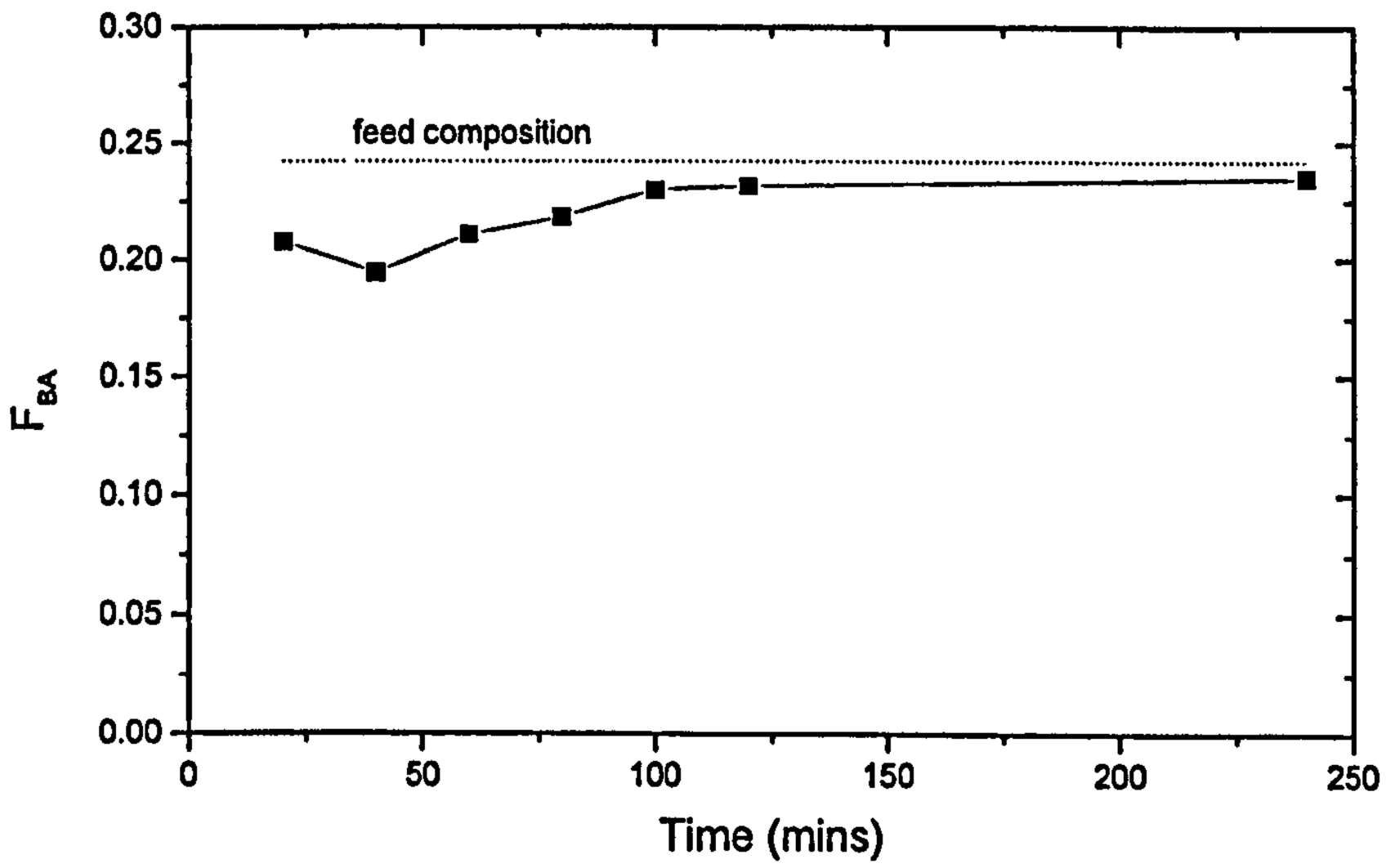

Figure 3.38 - *Fraction of butyl acrylate in the polymer synthesised in reaction MA7 versus time as measured by NMR.*

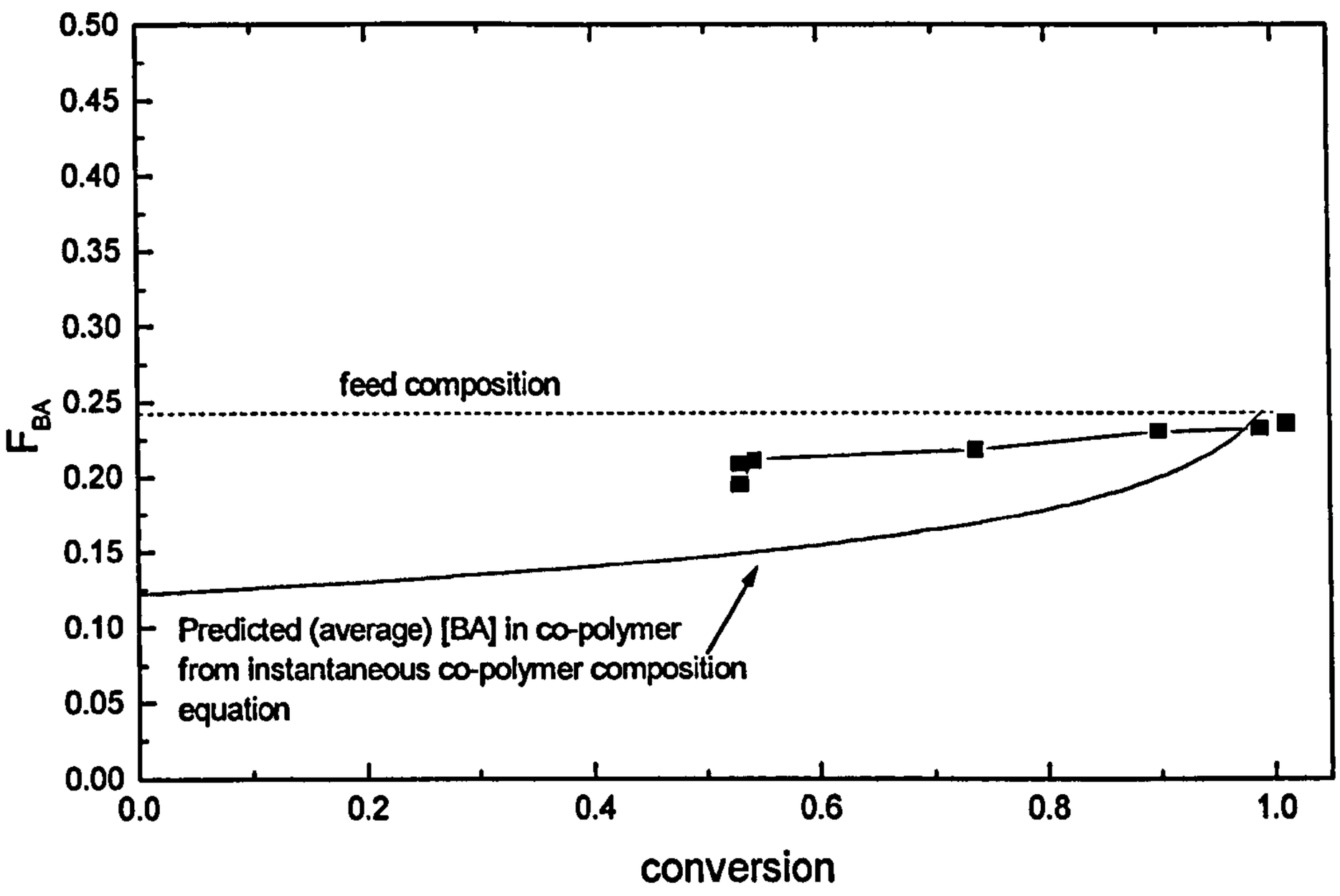

Figure 3.39 - *Fraction of butyl acrylate in the polymer synthesised in reaction MA7 versus instantaneous conversion as measured by NMR.*

Figure 3.39 compares the co-polymer composition measured by NMR to that predicted by the instantaneous co-polymer composition equation. As for the 50:50 ratio of monomers, early in the reaction the polymer is richer in butyl acrylate than predicted by the instantaneous co-polymer composition equation.

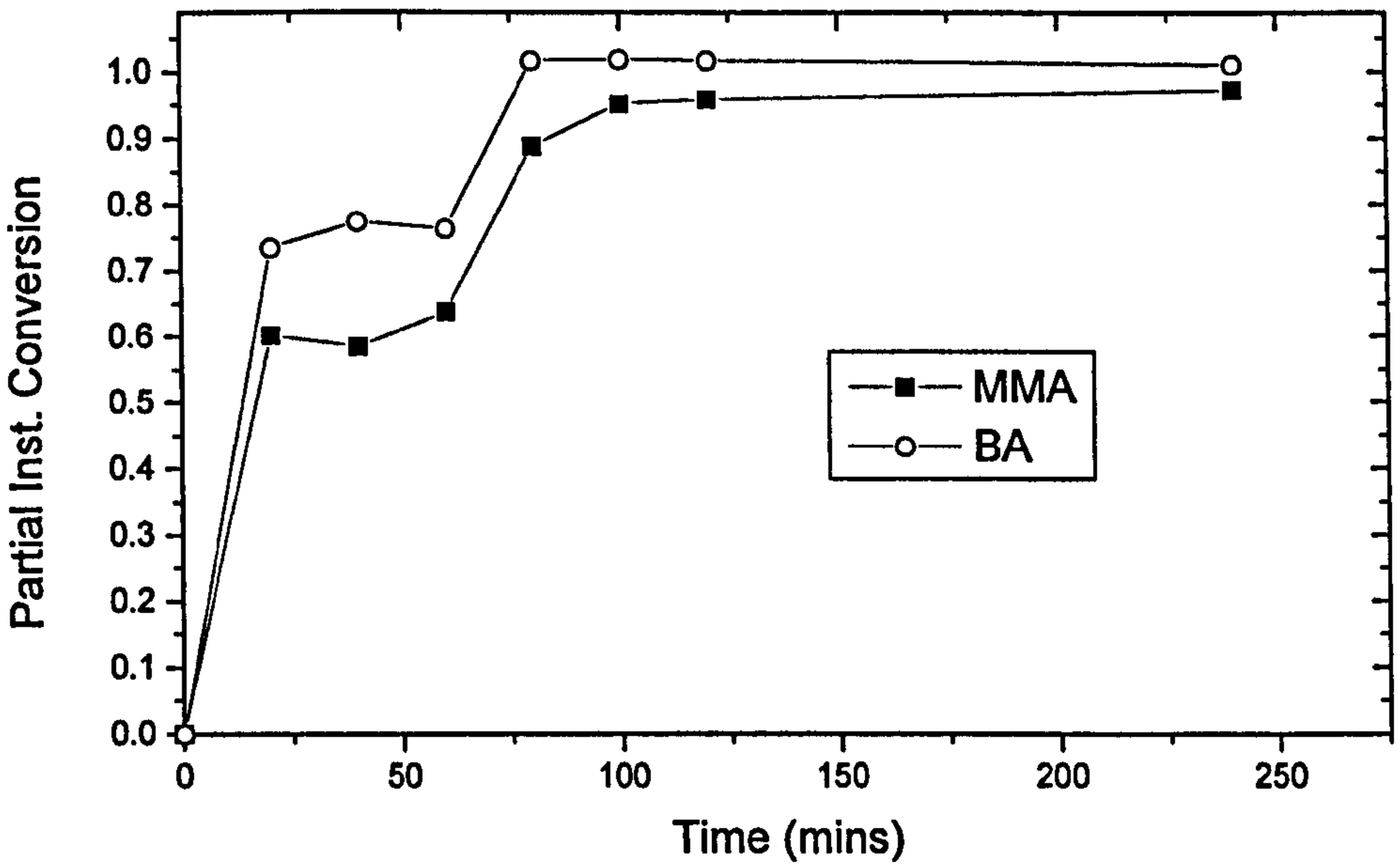

Figure 3.40 – *Partial monomer conversions (instantaneous) for experiment MA7*

The partial monomer conversions may be calculated from the NMR and gravimetric conversion results. It can be seen that as for the higher amount of butyl acrylate, shown in section 3.3.1, the methyl methacrylate is consumed faster than the butyl acrylate.

3.3.2.1 - DSC Analysis of MMA/BA (75:25 molar ratio) co-polymers

The glass transition temperatures of the polymers synthesised in section 3.3.2 were measured by differential scanning calorimetry.

Reaction	M_n	M_w	T_g onset / °C	T_g inflection / °C
MA6	10700	20000	35.9	46.0
MA7	13900	33500	41.4	46.4
MA8	26400	62600	46.8	53.7
MA9	177000	556000	49.5	57.8

Table 3.9 – *DSC results for MMA/BA Co-polymers (75:25 molar ratio) synthesised in emulsion polymerisations MA6-MA9*

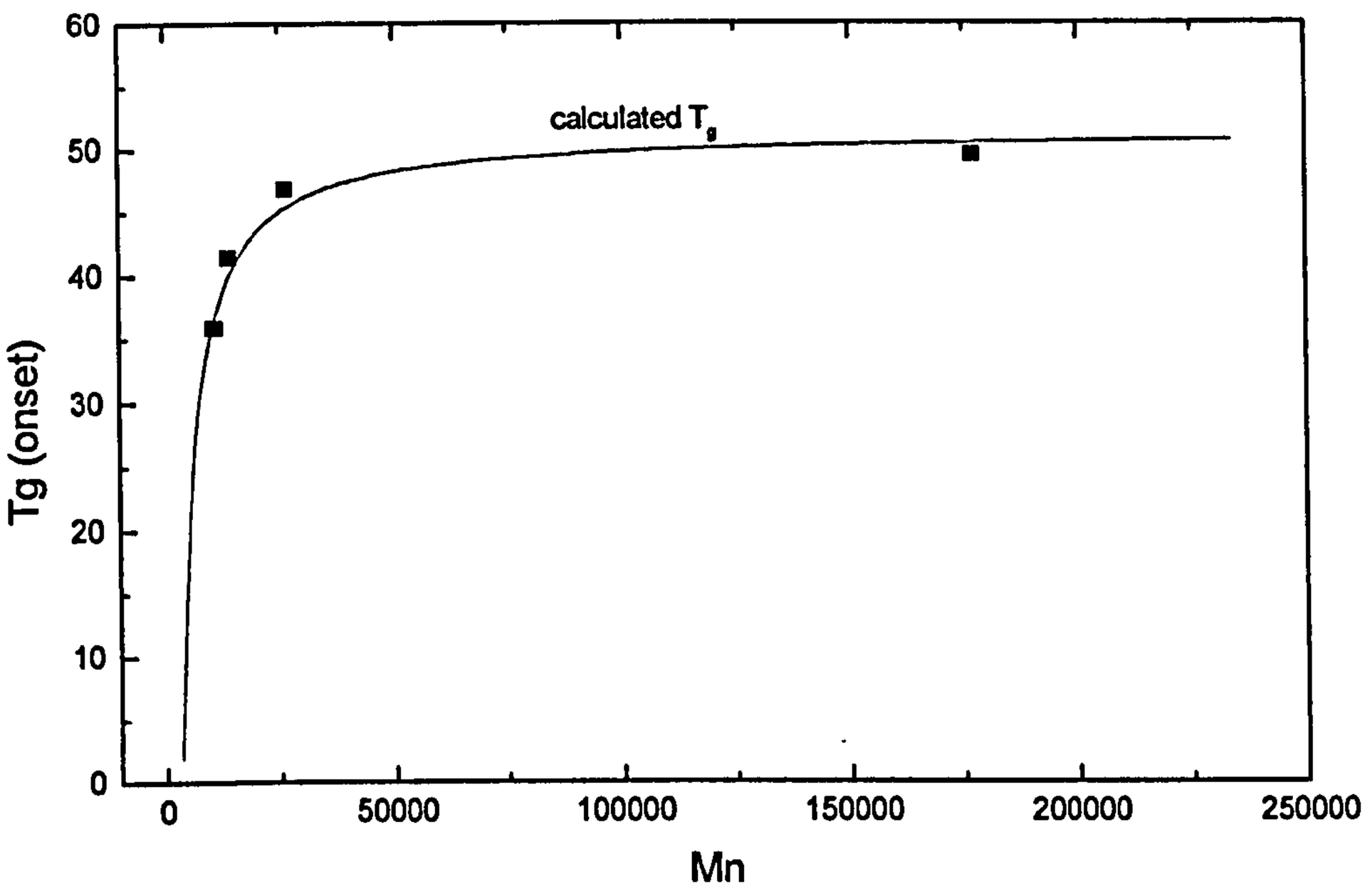

Figure 3.41 – *Glass transition temperature versus M_n for MMA/BA co-polymers (75:25 ratio of monomers)*

It was shown earlier that the relationship $T_g = T_{g\infty} - K/D_p$ could be used to predict the glass transition temperature of polymers, where $T_{g\infty}$ is the limiting

glass transition temperature at high molecular weight and K is a constant value. Using least squares analysis on the glass transition temperature for polymers made in reactions MA5-MA8 a $T_{g\infty}$ of 324 K (51 °C) and a K constant value of 1425 were obtained. The glass transition temperature of the MMA/butyl acrylate co-polymers are significantly lower than pure MMA polymers due to the lower glass transition temperature of the butyl acrylate.

3.3.3 MMA/BA (90:10 molar ratio)

A series of emulsion polymerisations were carried out on a 90:10 molar ratio of MMA/BA with different concentrations of CCT agent being employed.

Reaction	Wt. COBF (g)	Ppm COBF	Feed Conditions	Mn	PDi	Inst. Conv.	Cs^E
MA10	0.0316	38.89	100% fed	3120	1.87	1.037	848
MA11	0.0224	27.57	100% fed	4560	1.76	1.008	818
MA12	0.0101	12.43	100% fed	30100	2.30	1.042	275
MA13	0.0000	0.00	100% fed	133000	2.70	1.060	-

Table 3.10 – *End properties of MMA/BA (90:10 molar ratio) emulsion polymerisations.*

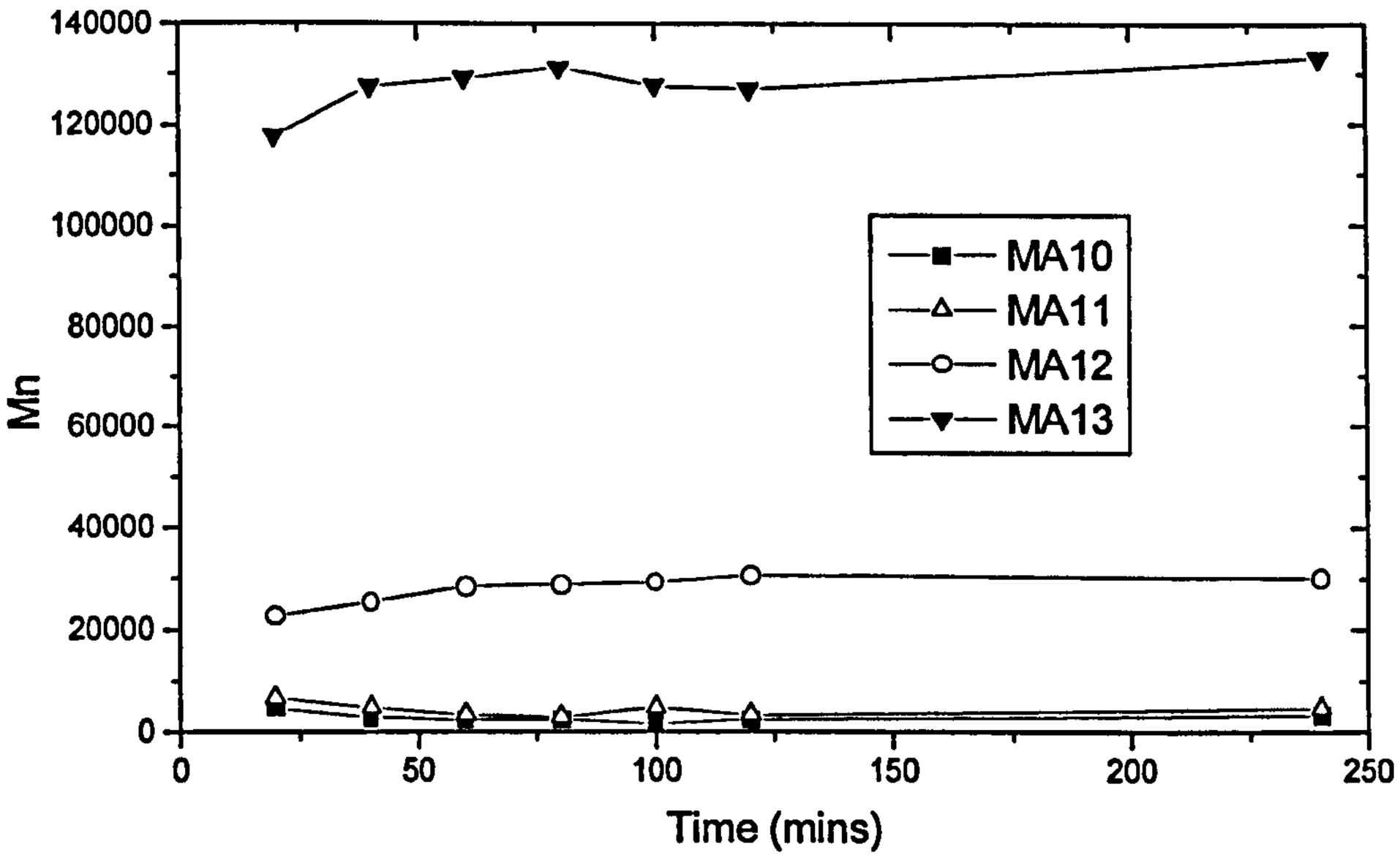

Figure 3.42 – *M_n versus time graph for emulsion polymerisations MA10-MA13*

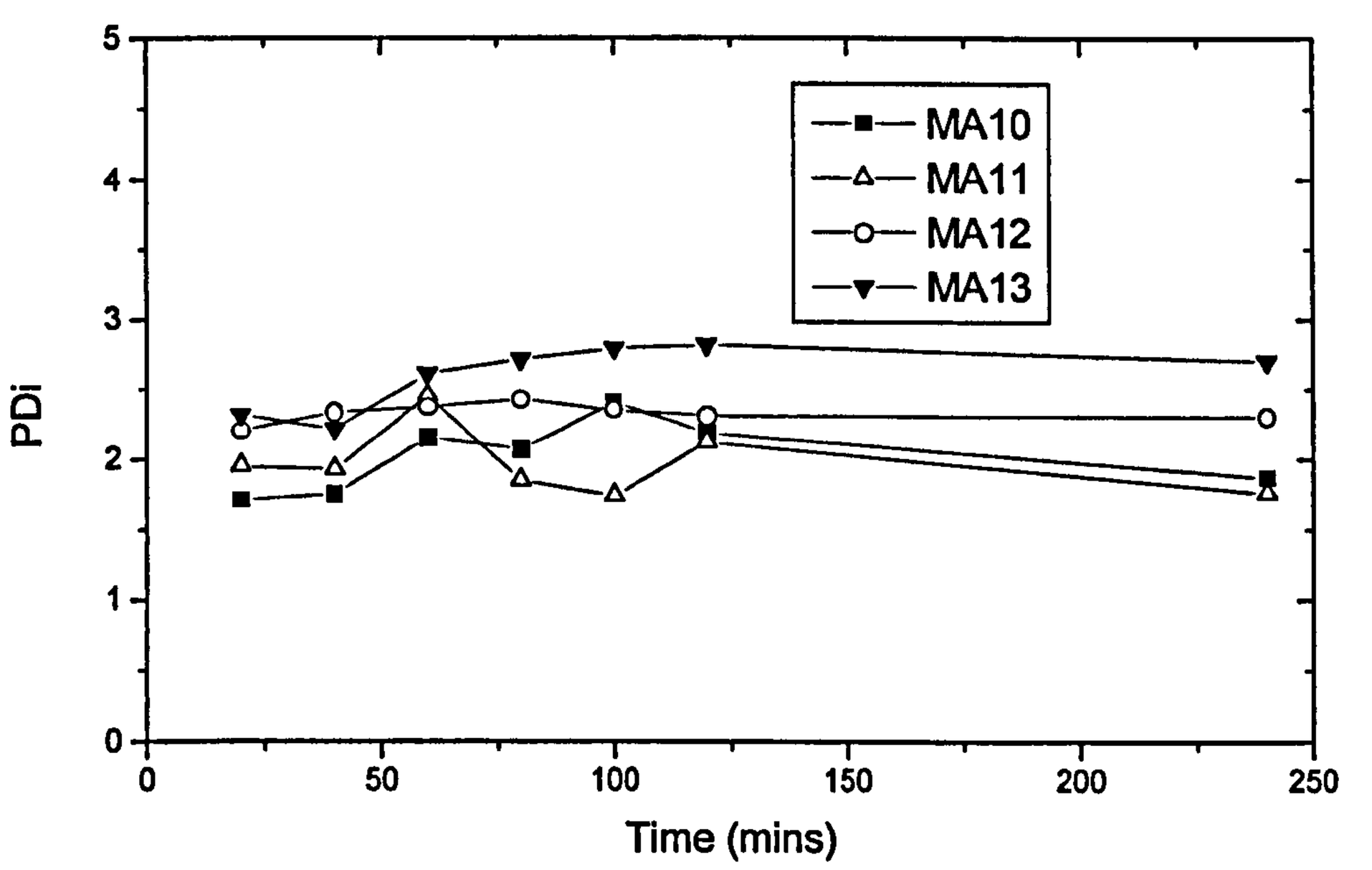

Figure 3.43 – *Polydispersity index versus time graph for emulsion polymerisations MA10-MA13*

Figures 3.42 and 3.43 show that with only a 10% addition of butyl acrylate to the MMA polymerisation there is not a significant effect on the polymerisation. The molecular weight stays low throughout the polymerisation for experiments MA10 and MA11 and there is even observed the threshold level of catalyst concentration for 10 ppm of COBF (MA12) where efficient CCT is not observed. The polydispersity index of the polymerisations all stay around 2 for the duration of the reaction.

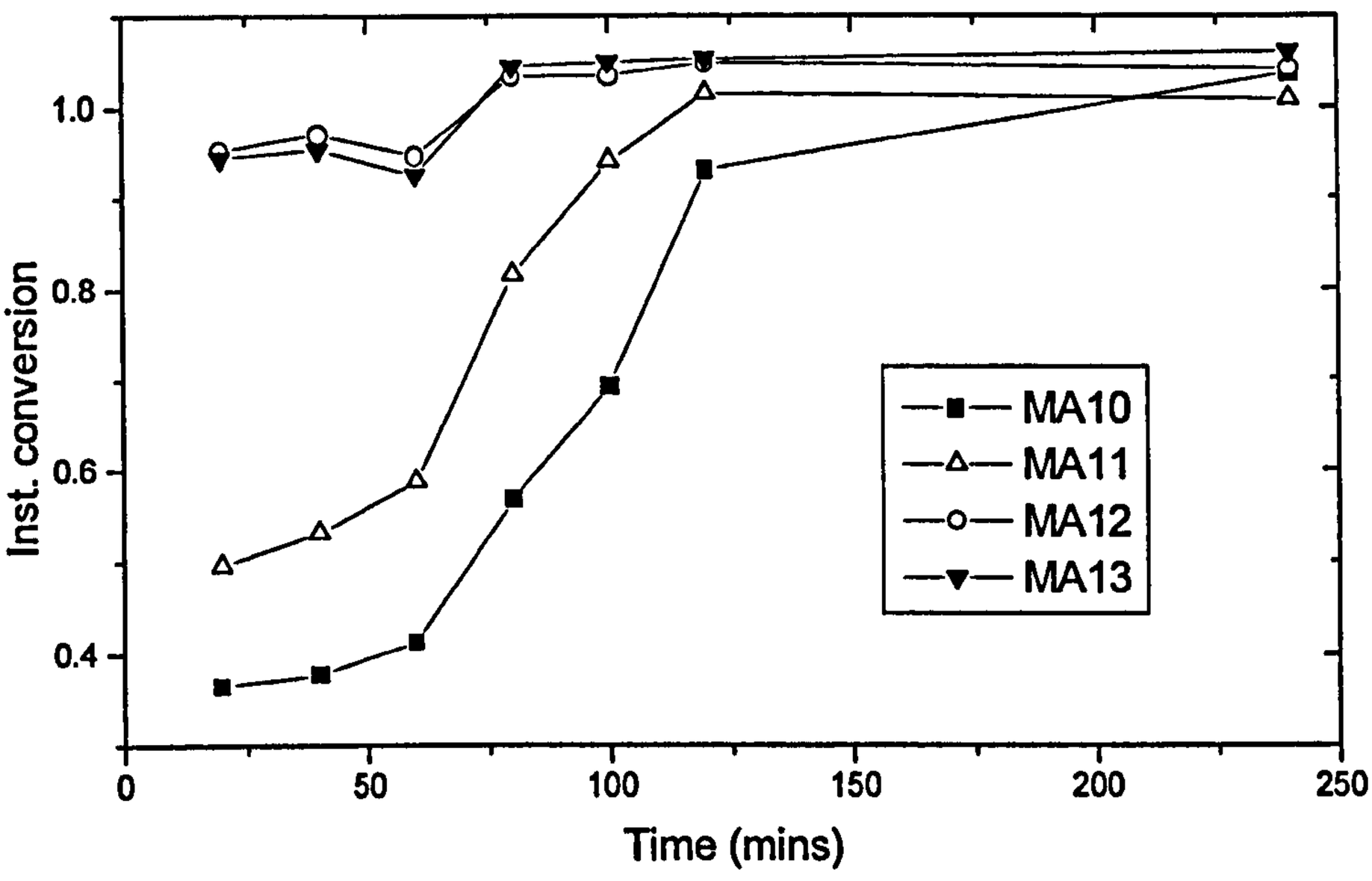

Figure 3.44 – *Instantaneous conversion versus time graph for emulsion polymerisations MA10-MA13*

The rates of polymerisation are very similar to the pure MMA polymerisations described in section 2.1 with the 10% butyl acrylate in the system not affecting the rate of reaction to any significant extent.

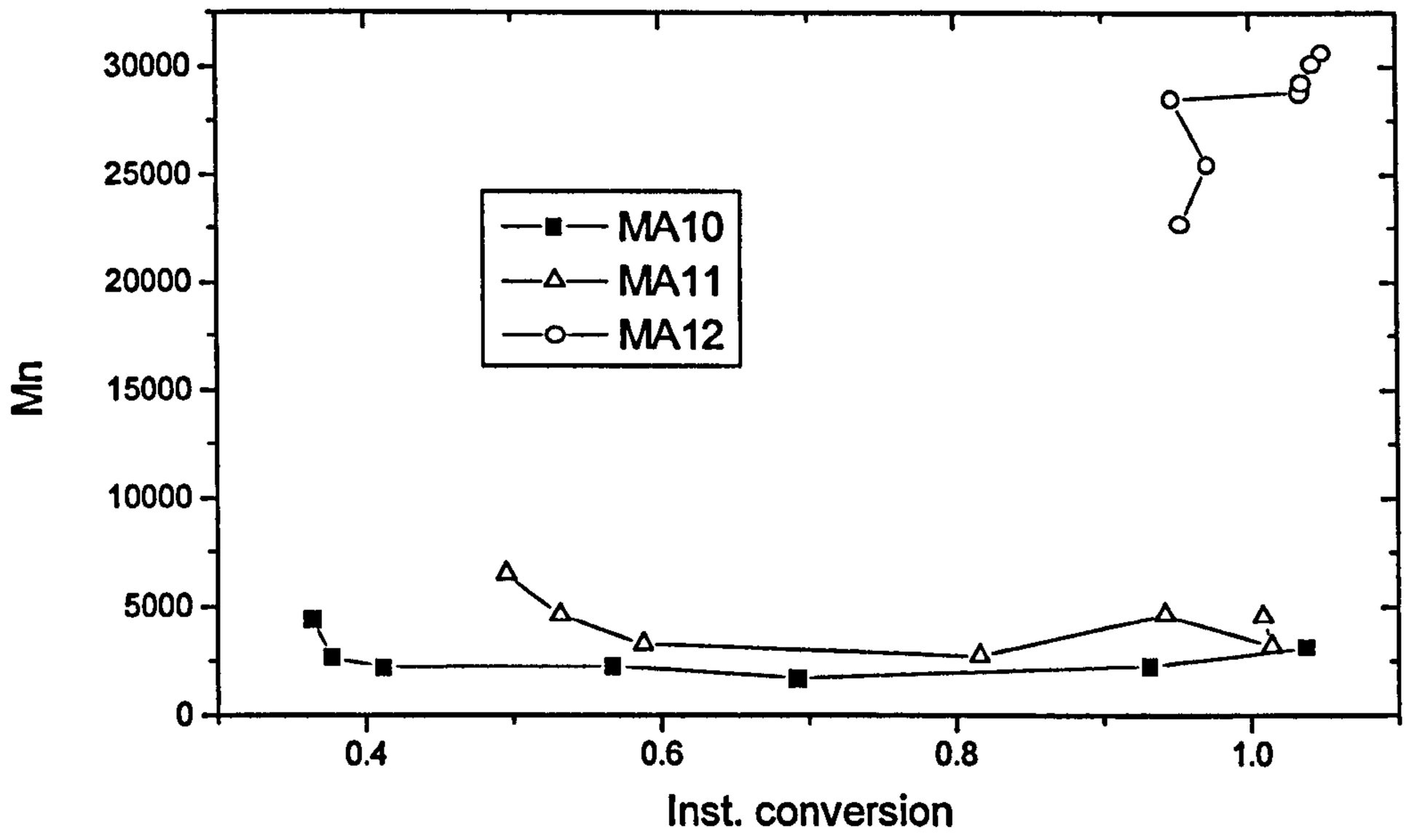

Figure 3.45 – *M_n versus instantaneous conversion graph for emulsion polymerisations MA10-MA12.*

In the M_n versus instantaneous conversion plot it can be seen that the large increase in molecular weight at the latter stages of the reaction observed for the higher ratios of butyl acrylate : methyl methacrylate does not occur.

If the instantaneous co-polymer composition is plotted for this monomer feed (figure 3.46) it can be seen that it is predicted that only at very high conversion will the amount of methyl methacrylate be reduced to a level where there is more BA than MMA.

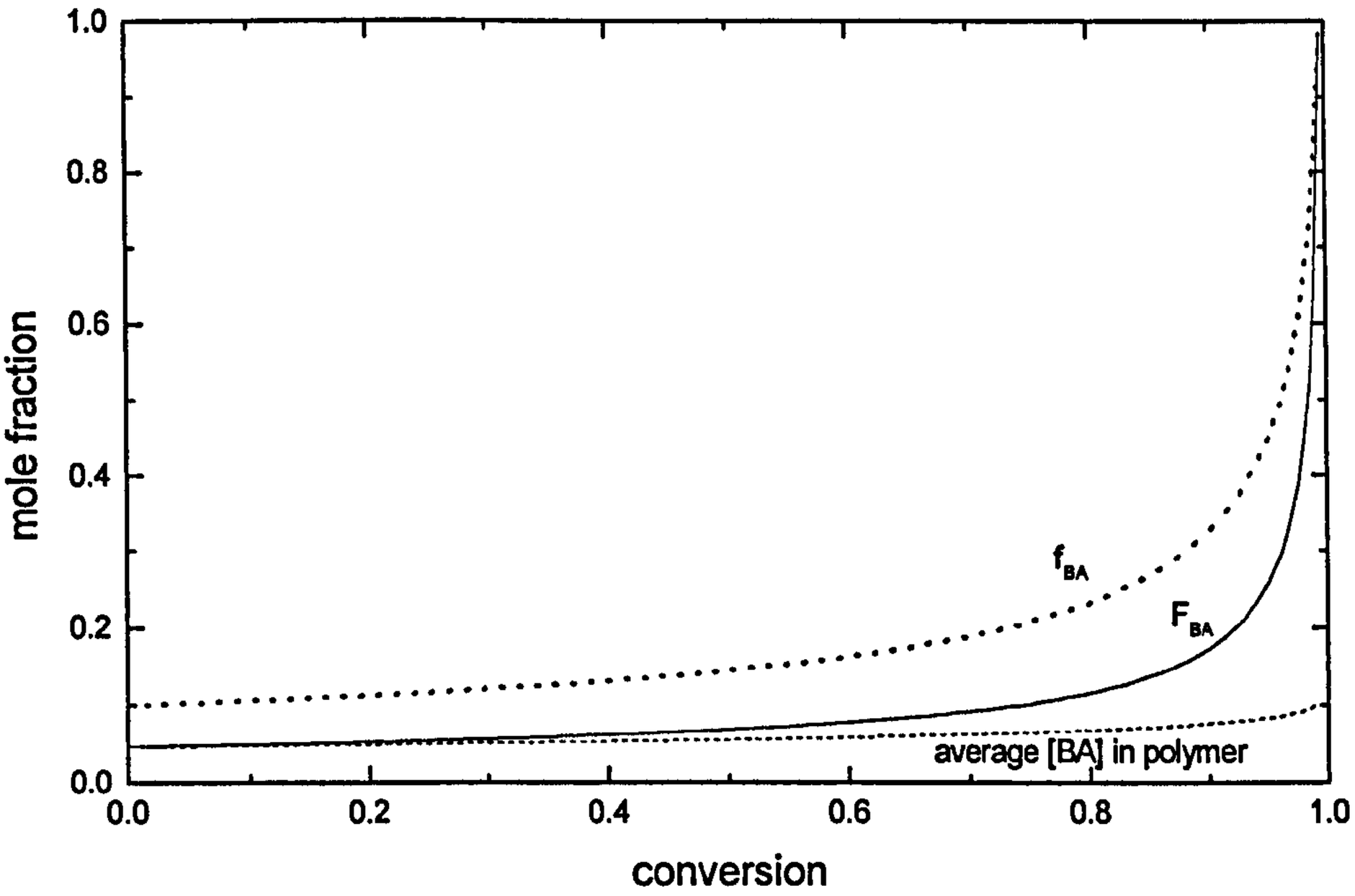

Figure 3.46 - *Calculated Instantaneous Co-polymer Composition for MMA/BA co-polymers (90:10 ratio of monomers)*

It is predicted that at 99% monomer conversion the remaining monomer is still composed of 65% MMA and 35% BA which is not significant enough to promote the grafting reaction.

3.3.3.1 DSC Analysis of MMA/BA (50:50 molar ratio) co-polymers

The glass transition temperatures of the polymers synthesised in section 3.3.3 were measured using differential scanning calorimetry and the results are shown in table 3.11

Reaction	M_n	M_w	T_g onset / °C	T_g inflection / °C
MA10	3120	5830	41.6	53.4
MA11	4560	8020	58.8	69.1
MA12	30100	69300	84.9	92.4
MA13	133000	360000	86.8	94.4

Table 3.11 - *DSC results for MMA/BA Co-polymers synthesised in emuslion polymerisations (90:10 molar ratio)*

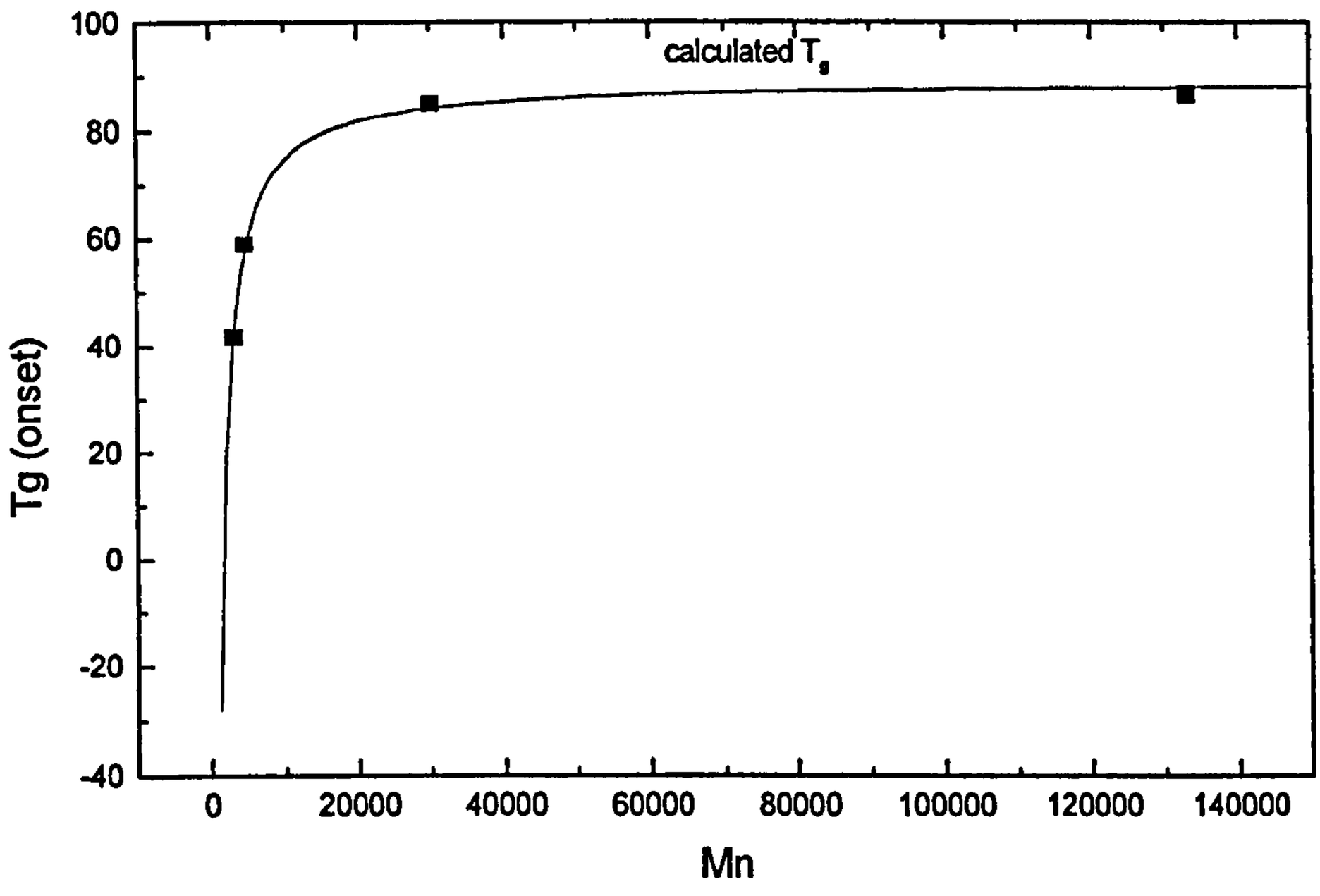

Figure 3.47 – *Glass transition temperature versus M_n for MMA/BA co-polymers (90:10 molar ratio)*

Again $T_g = T_{g\infty} - K/D_p$ was used to predict the glass transition temperature of these polymers (where $T_{g\infty}$ is the limiting glass transition temperature at high

molecular weight and K is a constant value). Using least squares analysis on the glass transition temperatures a $T_{g\infty}$ of 362 K (89 °C) and a K constant value of 1402 were obtained. The limiting glass transition is lower than for pure MMA (119 °C) due to the acrylate that has been added.

3.4 The CCT Emulsion Polymerisation of MMA/Methacrylic Acid

The synthesis of polymers containing methacrylic acid groups is of interest since polymers with such groups have the potential to be water soluble. For emulsion polymerisation to be carried out water insoluble monomers must be employed and so in order synthesise methacrylic acid containing polymers by emulsion polymerisation a non-water soluble monomer must be used as a co-monomer. This section endeavours to determine whether it is possible to synthesise MMA/methacrylic acid containing macromonomers by catalytic chain transfer emulsion polymerisation. Limited data has been published in the patent literature on the synthesis of MMA/methacrylic acid macromonomers[10] and this section also aims to expand on this data. The target polymer is shown in figure 3.48.

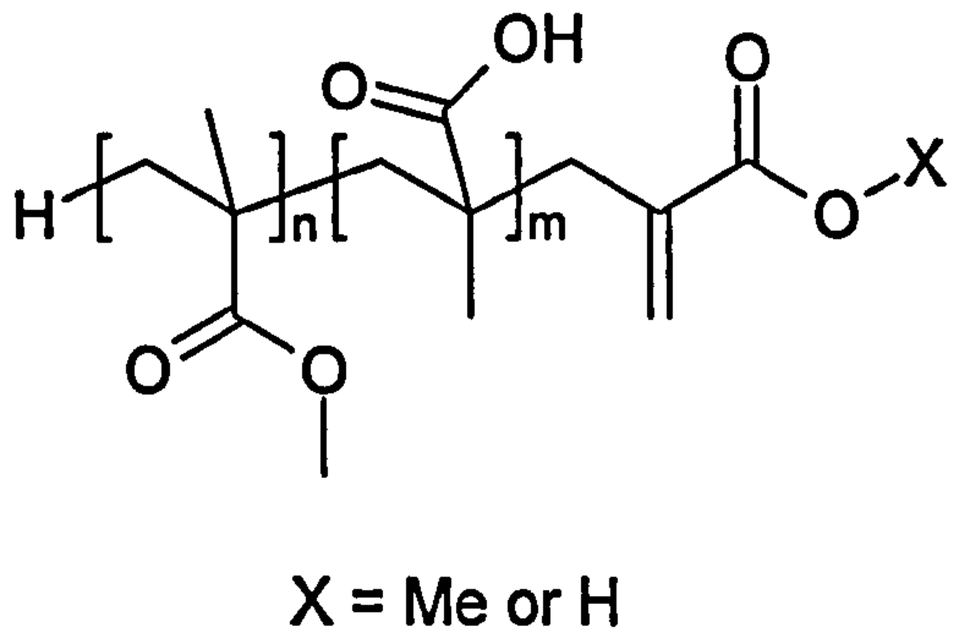

Figure 3.48 – *Structure of MMA/Methacrylic acid statistical co-polymer made by CCT.*

3.4.1 MMA/Methacrylic Acid (90:10 molar ratio)

A 90:10 mixture of MMA and methacrylic acid was polymerised in an attempt to synthesise macromonomers with that composition.

Reaction	Wt. COBF (g)	Ppm COBF	Feed Conditions	Mn	PDI	Inst. Conv.	Cs^E
MC1	0.0325	37.99	100% fed	2150	1.73	1.005	1211
MC2	0.0203	23.73	100% fed	3150	3.32	1.038	1320
MC3	0.0150	17.53	100% fed	4630	1.81	1.036	1217
MC4	0.0115	13.44	100% fed	5660	2.42	1.053	1298

Table 3.12 – *End properties of MMA/Methacrylic acid polymerisations (90:10 molar ratio)*

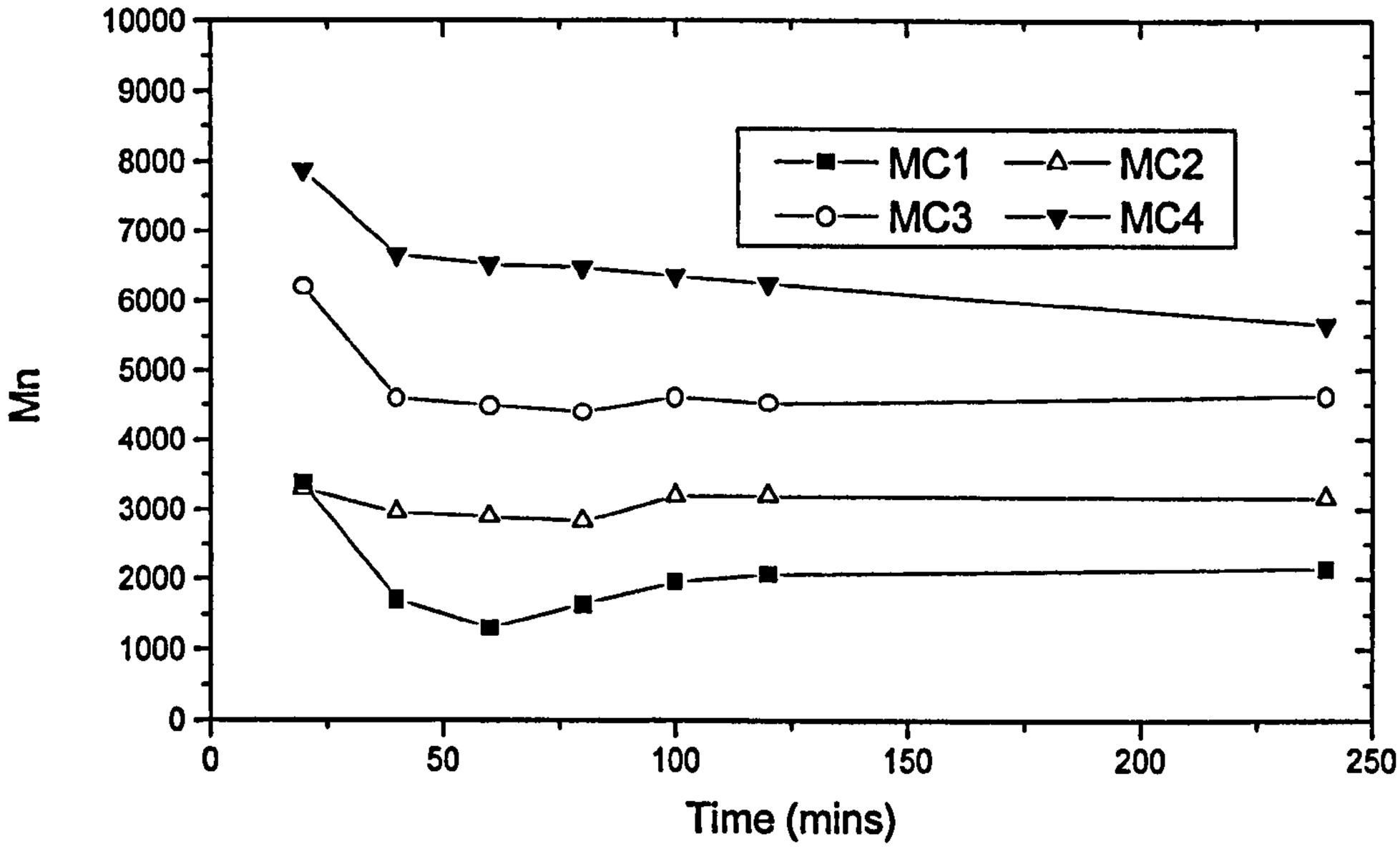

Figure 3.49 – *M_n versus time graph for emulsion polymerisations MC1-MC4*

The molecular weight data shown in figure 3.49 shows that for a 90:10 mixture of MMA/methacrylic acid effective macromonomer synthesis has been carried out. The number average molecular weight of the polymers formed varies with amount of CCT agent present in the polymerisation , which is as expected for effective macromonomer synthesis. The polydispersity indices of the polymers formed for reactions MC2 and MC4 are slightly higher than normal, but this may be due to interaction between the methacrylic acid groups on the polymer and the SEC separation column.

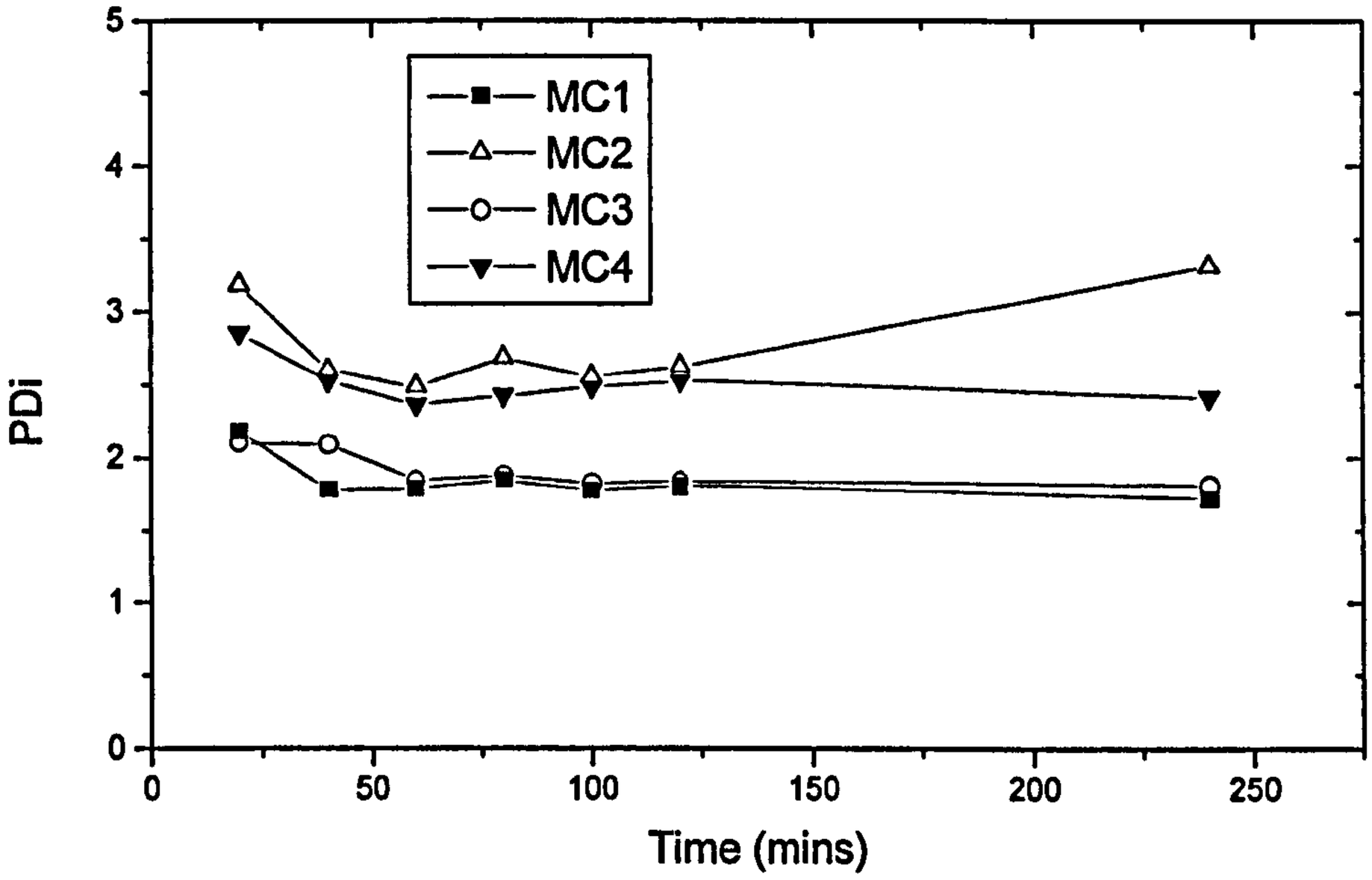

Figure 3.50 – *Polydispersity index versus time graph for emulsion polymerisations MC1-MC4*

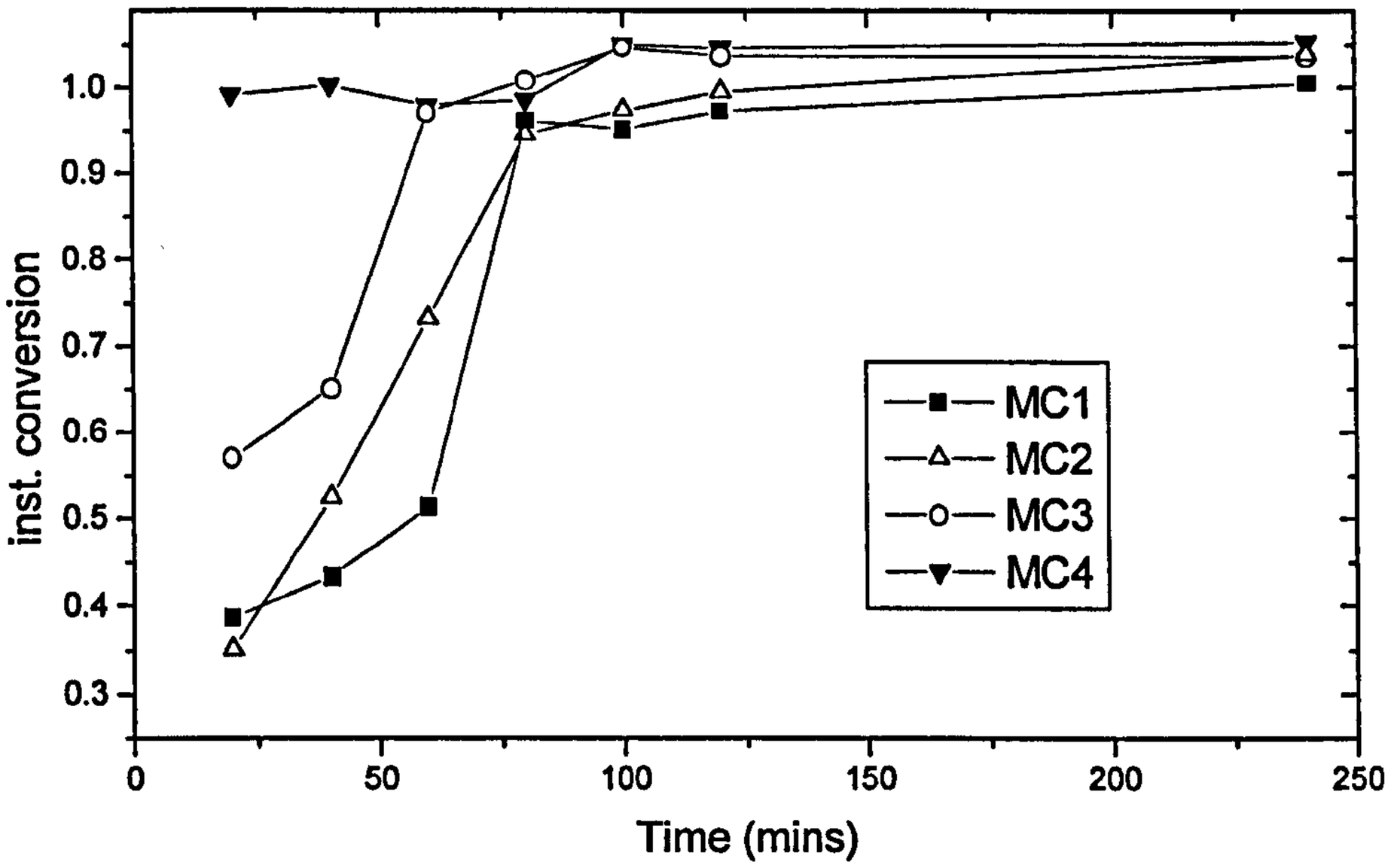

Figure 3.51 – *Instantaneous conversion versus time graph for emulsion polymerisations MC1-MC4*

The rates of reaction for experiments MC1, MC2 and MC3 are very similar to that for the pure MMA reactions as would be expected. Reaction MC4 is unusual in the fact that it appears to be under starved fed conditions but the CCT reaction is still operating at full efficiency with the Cs^E value being close to that for the other reactions. It was found that on the addition of ammonium hydroxide base to the emulsion that the polymer was insoluble and so a greater amount of methacrylic acid is necessary for the polymer to become base soluble.

3.4.2 MMA/Methacrylic Acid (70:30) molar ratio

In order for the MMA/methacrylic acid co-polymers to be soluble in base more than 10% methacrylic acid is required. A series of emulsion polymerisations were performed using a 70:30 mixture of the two monomers.

Reaction	Wt. COBF (g)	Ppm COBF	Feed Cond.	Mn NMR	Mn GPC	Inst. Conv.	Cs^E NMR	Cs^E SEC*
MC5	0.035	39.15	100% fed	10400	17500	1.007	235	140
MC6	0.021	23.49	100% fed	11200	19400	1.027	366	211
MC7	0.010	11.19	100% fed	15200	18700	1.041	564	459

*Polymers from these reactions were first methylated before SEC performed.

Table 3.13 – *End properties of MMA/methacrylic acid (70:30 molar ratio) polymerisations*

It can be seen from the data in table 3.13 that the increase in the amount of methacrylic acid from 10% to 30% has had a large effect on the CCT reaction. The molecular weights are much higher than for the equivalent reaction with only 10% methacrylic acid present and the reactions appear to be much less controlled. It has been shown previously that hydrolysis of the COBF catalyst will occur at low pH[11] and it is likely that the higher amount of methacrylic acid

in the system slowly hydrolyses the catalyst through the reaction, lowering the concentration of transfer agent in the emulsion.

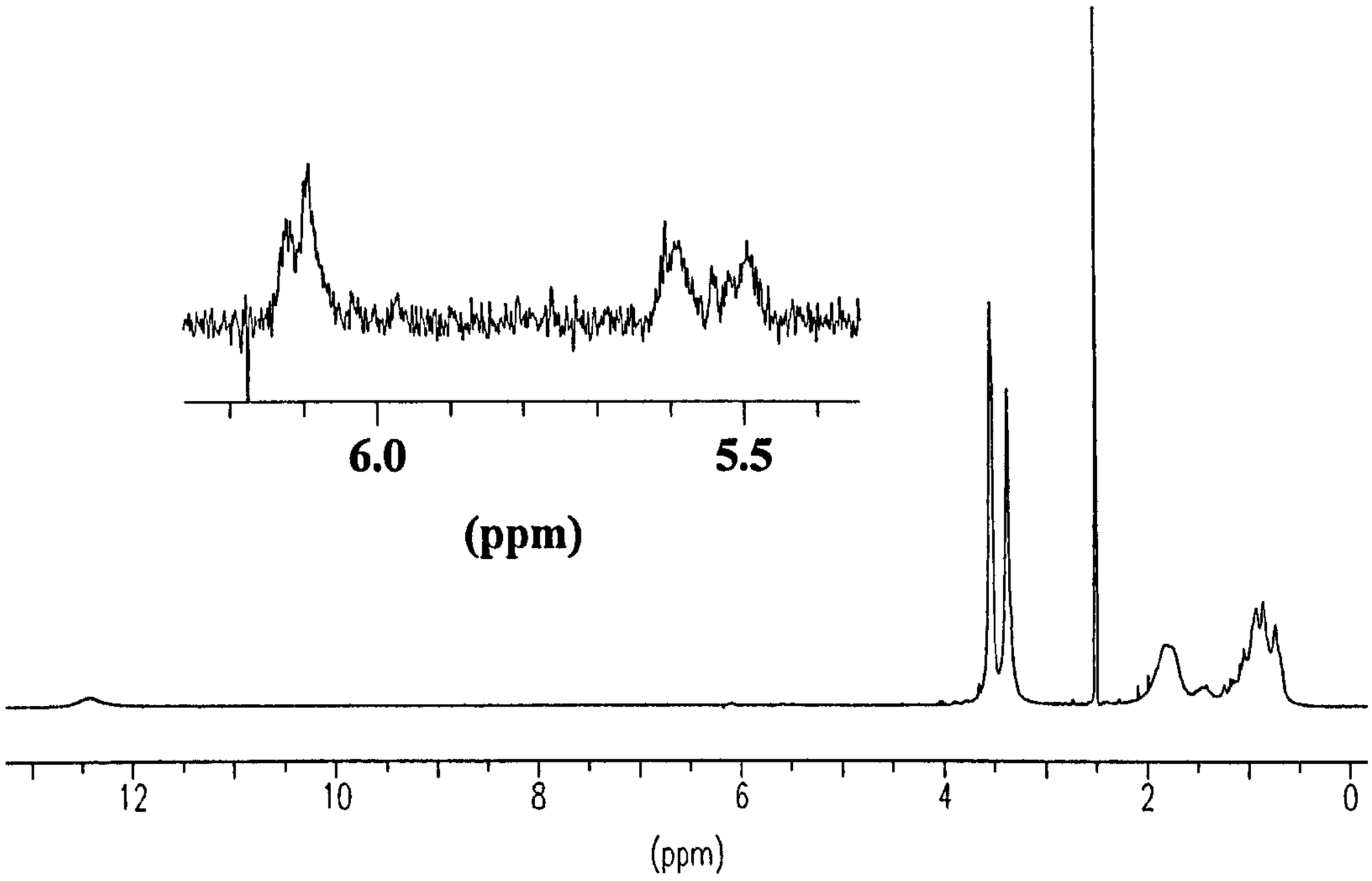

Figure 3.52 – *^{1}H NMR spectrum (d-6 DMSO as solvent) of MMA/methacrylic acid macromonomer synthesised in CCT emulsion polymerisation MC2*

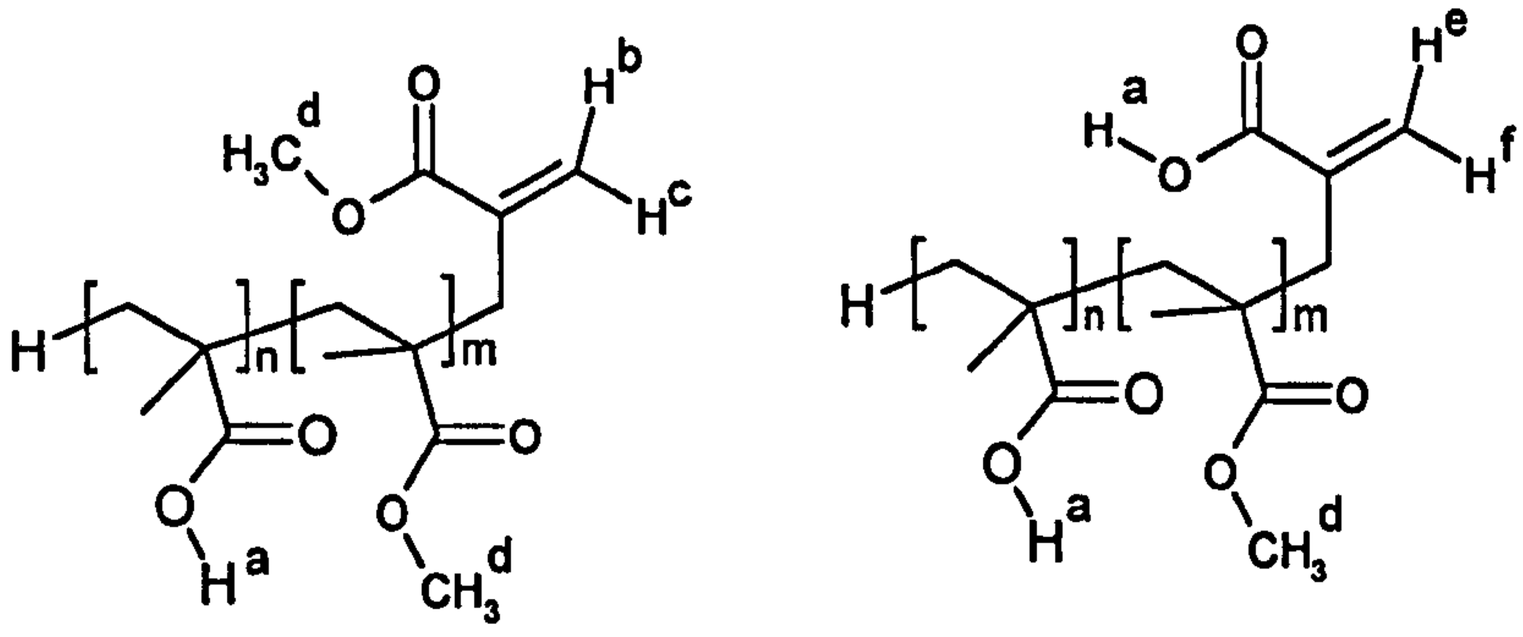

Figure 3.53 – *Structure of MMA/methacrylic polymer with protons labelled for NMR analysis*

Peak (ppm)	Integral	Multiplet Type	Assignment
12.43	328.7	Singlet (broad)	Acid proton [a]
6.10	10.00	Singlet	Vinyl protons [b] and [e]
5.56	10.15	Singlet	Vinyl protons [c] and [f]
3.54	2527.5	Singlet	Methoxy proton [d]
3.37	-	Singlet	Residual water protons
2.50	-	Quintet	DMSO (solvent) protons
0.5-2.5	6239.1	-	In chain CH_2 and CH_3 protons

Table 3.14 – *Assignments for NMR spectrum in figure 3.52*

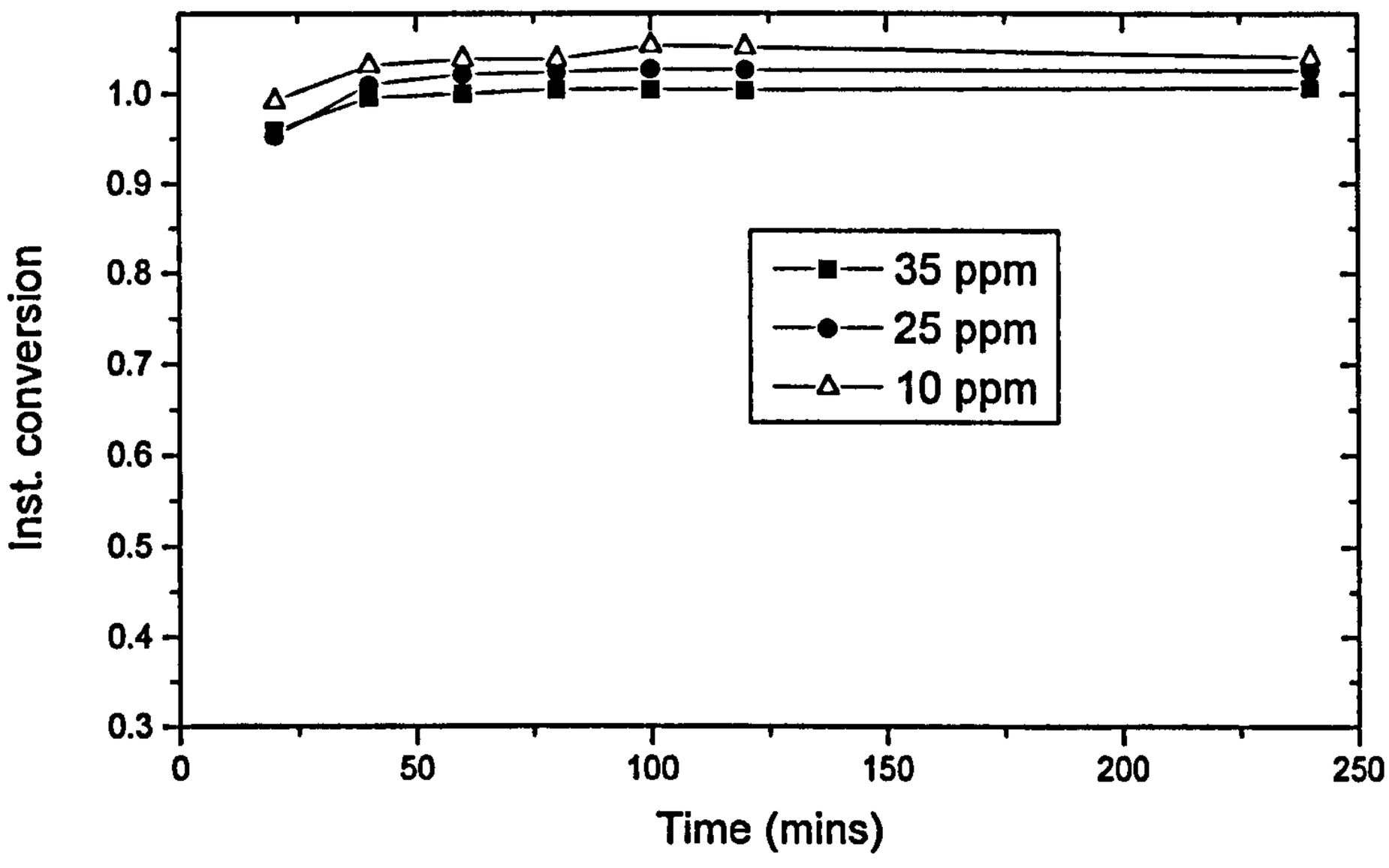

Figure 3.54 – *Instantaneous conversion versus time graph for emulsion polymerisations MC5-MC7*

The conversion data for these reactions are shown in figure 3.54 and they show that the reactions are fast with the polymerisations always being over 95%

instantaneous conversion. The fact that the polymerisations are so fast is probably due to the low effective catalyst concentration due to COBF hydrolysis. Although the polymerisations are not as predictable as would be hoped for and so although a particular molecular weight cannot be targeted, the reaction is still useful for the synthesis of methacrylic acid containing macromonomers. Unlike for the 90:10 ratio of MMA : methacrylic acid the polymers synthesised in these reactions are soluble in base. The results shown are in contradiction with the patent data[10] where it was published that very low molecular weight polymers could be synthesised using CCT emulsion polymerisation. It is possible that the MMA/methacrylic acid polymers interacted with the SEC column used to determine molecular weight giving an M_n value lower than was actually the case.

3.4.3 MMA/Methacrylic Acid (80:20) molar ratio

In an attempt to synthesise base soluble MMA/Methacrylic acid macromonomers in a controlled fashion an 80:20 mixture of MMA/methacrylic acid was employed.

Reaction	Wt. COBF (g)	Ppm COBF	Feed Conditions	Mn	PDI	Inst. Conv.	Cs^E
MC8	0.034	38.74	100% fed	16718*	-	1.049	150
MC9	0.022	24.62	100% fed	19493*	-	1.064	202

*Polymers were first methylated before SEC was performed (see section 5.2.3)

Table 3.15 – *End properties for MMA/methacrylic acid (80:20 molar ratio) emulsion polymerisations*

As for the 70:30 mixture of monomers the CCT emulsion polymerisations for 80:20 (MMA:methacrylic acid) appear to be less controlled than for the 90:10 macromonomomers. Once again the Cs^E value is greatly reduced from that for the pure MMA reactions, this suggests that the acidic monomer is destroying the catalyst.

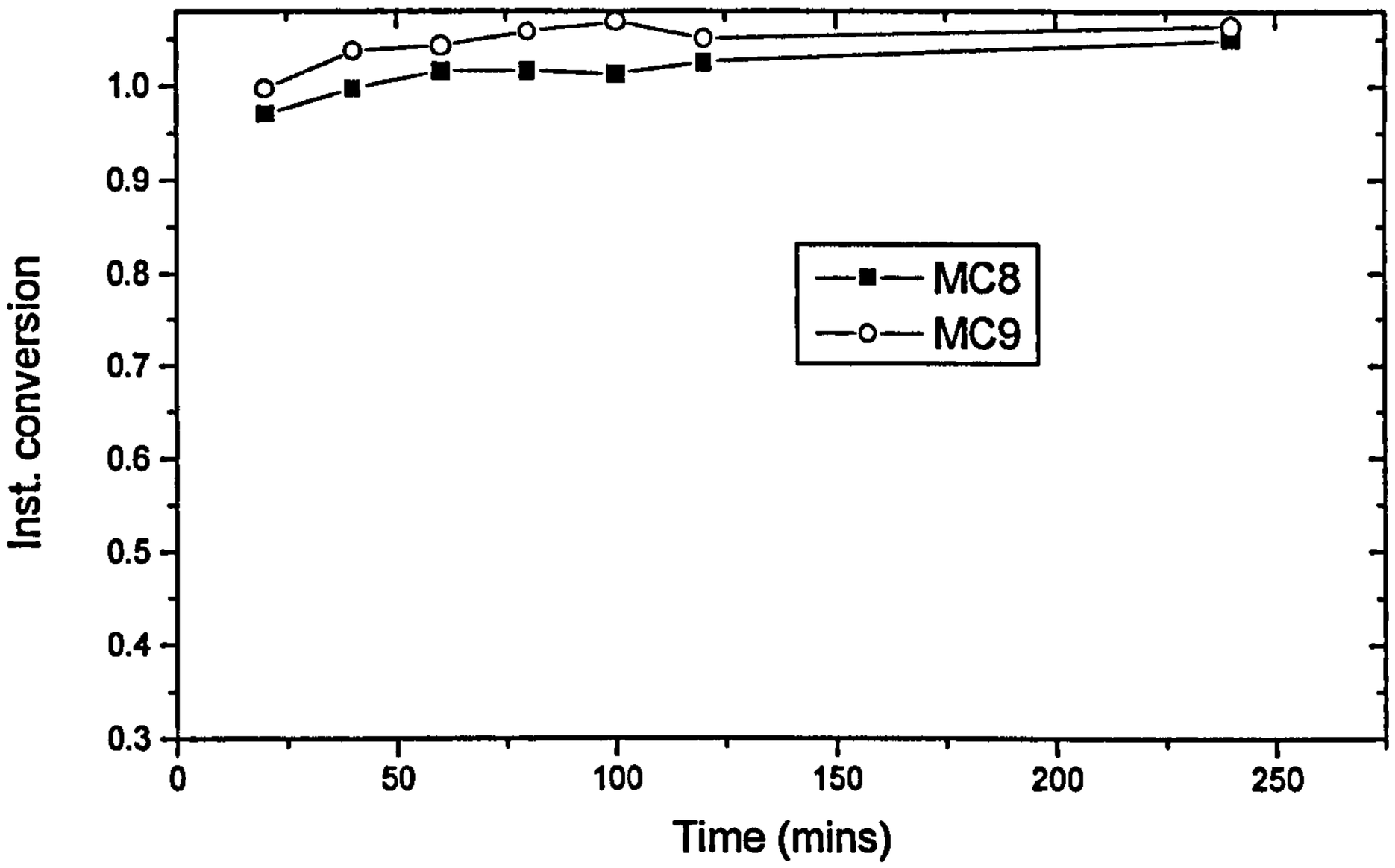

Figure 3.55 – *Instantaneous conversion versus time graph for emulsion polymerisations MC8 and MC9*

The rates of reaction as shown in figure 3.55 are very similar to the reactions shown in section 3.3.2, the reactions being under starved fed conditions.

On the addition of ammonium hydroxide base to the final latex it was found that the polymer was soluble at the high pH.

3.5 Conclusions

The synthesis of co-polymers by CCT in emulsion has been described. It has been shown in this chapter that the addition of the water soluble methacrylate monomer HEMA to a MMA CCT emulsion polymerisation had little effect on the transfer reaction. Macromonomers consisting of a statistical mixture of MMA and HEMA can be easily prepared by CCT emulsion although a 50:50 ratio of the monomers does not produce a stable latex.

The results of CCT emulsion polymerisations where the synthesis of butyl acrylate/ methyl methacrylate macromonomers were attempted were also outlined in this chapter and effective macromonomer synthesis was observed for low amounts of acrylate. For higher amounts of acrylate it was observed that effective macromonomer synthesis was only observed up to moderate conversions where at high conversions residual acrylate underwent reaction with macromonomer synthesised earlier in the reaction forming graft co-polymer.

The synthesis of methacrylic acid containing macromonomers using CCT emulsion polymerisation was studied and it was shown that controlled macromonomer synthesis could only be carried out at low methacrylic acid concentrations. At higher methacrylic acid : MMA ratios a low transfer constant was observed suggesting a destruction of the catalyst by the acidic monomer.

3.6 References

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Chapter 4

CCT Emulsion Polymerisation Using New Catalysts

4.1 Introduction

It has been shown in previous chapters that the synthesis of methacrylate containing macromonomers can be easily achieved by utilising the process of Catalytic Chain Transfer under emulsion polymerisation conditions. The catalyst used in all polymerisations reported so far in this thesis has been COBF, however it is quite simple to substitute the methyl groups of this CCT agent and replace them with other groups in order to synthesise a wider range of catalysts based on the structure shown in figure 4.1.

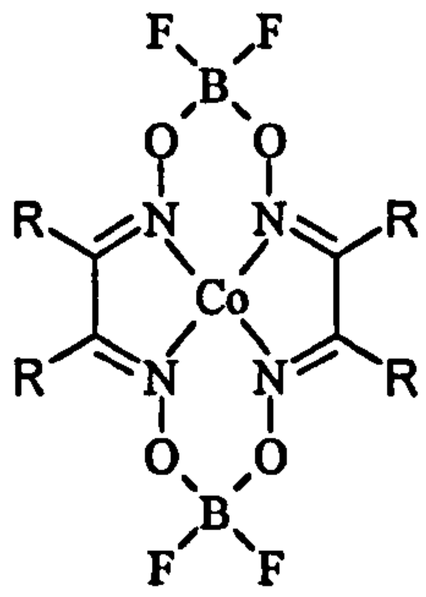


Figure 4.1 – *General structure of Cobalt CCT Agents*

The structure of the catalytic chain transfer agent used in a polymerisation has been shown to have not only an effect on the transfer activity but also on the hydrolytic stability of the catalyst and the tolerance to oxygen [1-5]. Various

cobalt CCT compounds have been utilised in bulk or solution polymerisation of methacrylate monomers and it has been shown that structures based on that shown in figure 4.1 afford the catalyst high activity and stability with low cost[6]. Changing the structure of the CCT agent COBF has been shown to have an affect on the transfer activity of the catalyst[7]. By changing the structure of the catalyst, the cross sectional area is affected and since CCT is believed to be a diffusion controlled process (see section 1.7) the cross sectional area may have an effect on the diffusion coefficients and hence activity of the catalyst.

The effect of catalyst structure on CCT emulsion polymerisation has been shown by Kukulj et al[8]. A very hydrophobic catalyst, where all the methyl groups of COBF were replaced by phenyl groups, was compared to COBF itself. The hydrophobic catalyst was considerably less effective at reducing molecular weight than COBF and this was ascribed to the inability of the hydrophobic catalyst to transport between particles since it has a negligible water solubility.

In work parallel to research contained ion this thesis a number of catalysts were synthesised *[1] by a modified published procedure[4]. These catalysts were used to determine the structural effect of the CCT catalyst on the transfer activity in bulk and solution polymerisations. It was decided to employ some of these catalysts in emulsion polymerisations in order to determine the effect of the catalyst structure under these conditions.

* Syntheses carried out by J.L.Waterson, S.F.Bon and R.Harrison at the University of Warwick

The results of the emulsion polymerisations using these CCT agents are described in the following section. The change in nature of the R groups will have two possible effects in an emulsion polymerisation.

i) An effect on the transfer activity of the catalyst either by a steric or an electronic effect.

ii) An effect on the solubility of the catalyst in the separate phases of the emulsion polymerisation effecting the concentration of the catalyst at the locus of polymerisation and hence the observed transfer constant.

4.2 Co(II) catalysts

A series of catalyst were employed in emulsion polymerisations with increasing size of alkyl chain attached to the glyoxime part of the transfer agent.

Catalyst (1)

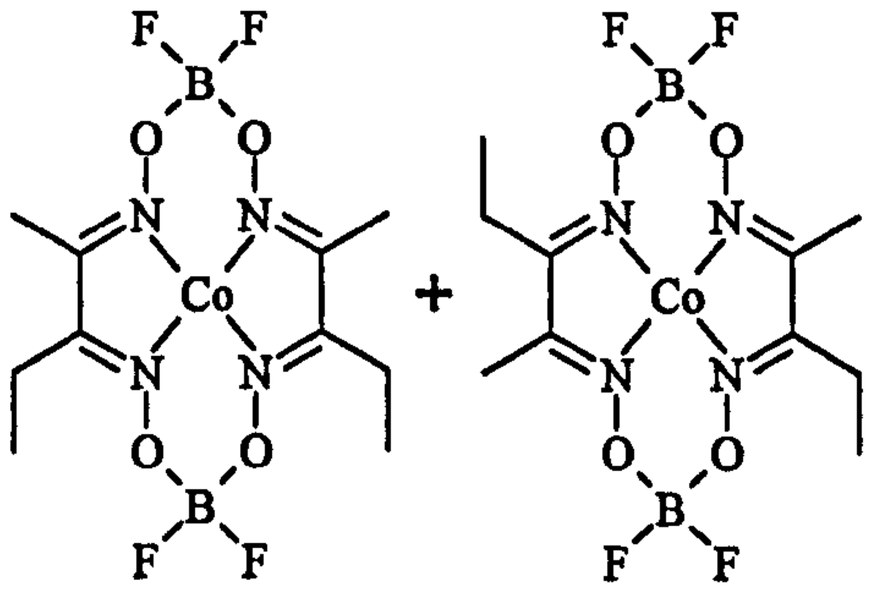


Figure 4.2 – *Structure of Catalyst (1)*

Reaction	Wt. COBF (g)	Ppm COBF	Feed Conditions	Mn	PDi	Inst. Conv.	Cs^E
(1)	0.0177	19.85	100% fed	2260	1.88	1.010	2233

Table 4.1 – *End conditions for emulsion polymerisation (1)*

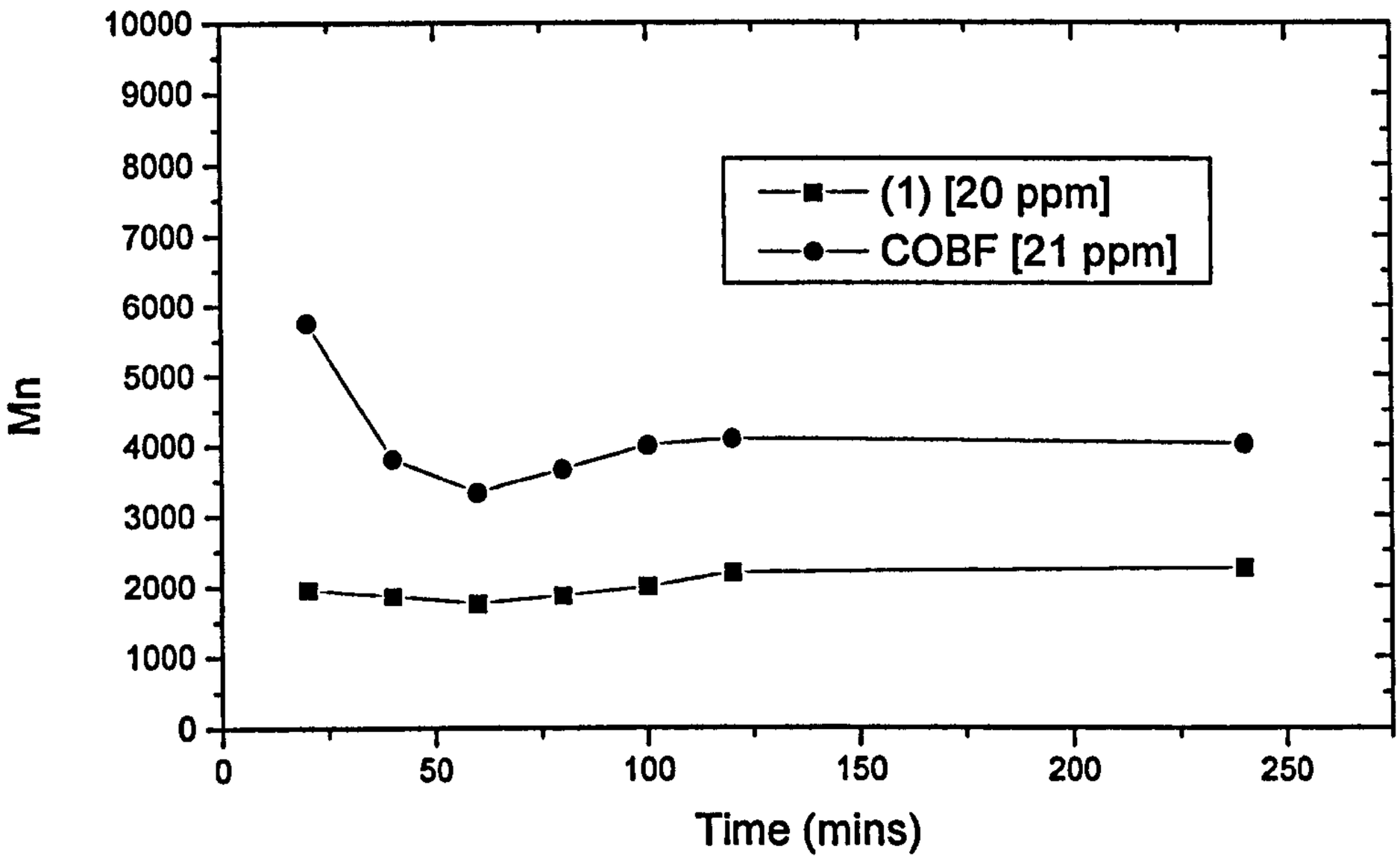


Figure 4.3 – *M_n versus time graph for polymerisations (1)*

It can be seen in figure 4.3 that when approximately the same concentration of cobalt catalyst is used (based on moles transfer agent : moles monomer) that a lower molecular weight is observed for catalyst (1) than for COBF, showing that it has a higher transfer constant in the emulsion polymerisation of MMA (Cs^E). The partitioning of the catalyst is such that $[(1)]_{MMA}/[(1)]_{aq} = 8.09$ [9]. It can be seen that the catalyst is much more soluble in the monomer phase than the water phase. It was shown in chapter 1 that $[COBF]_{MMA}/[COBF]_{aq} = 0.69$ and so

catalyst (1) has a higher concentration in the particles than COBF. The chain transfer constant of catalyst (1) in the bulk polymerisation of MMA at 60 °C is lower than for COBF with a Cs for catalyst (1) = 12 300 [9] and a Cs for COBF = 40 000 [10]. It can be seen that the partitioning of the catalyst has a large effect on the activity of the catalyst in emulsion. Even though catalyst (1) has a lower transfer constant than COBF the fact that there is more of the catalyst present at the site of polymerisation results in a higher activity in emulsion. Also since it is postulated that catalyst is destroyed in the aqueous phase by the acidic initiator, the lower concentration of catalyst in the aqueous phase may mean a lower rate of destruction and a higher observed transfer constant being observed.

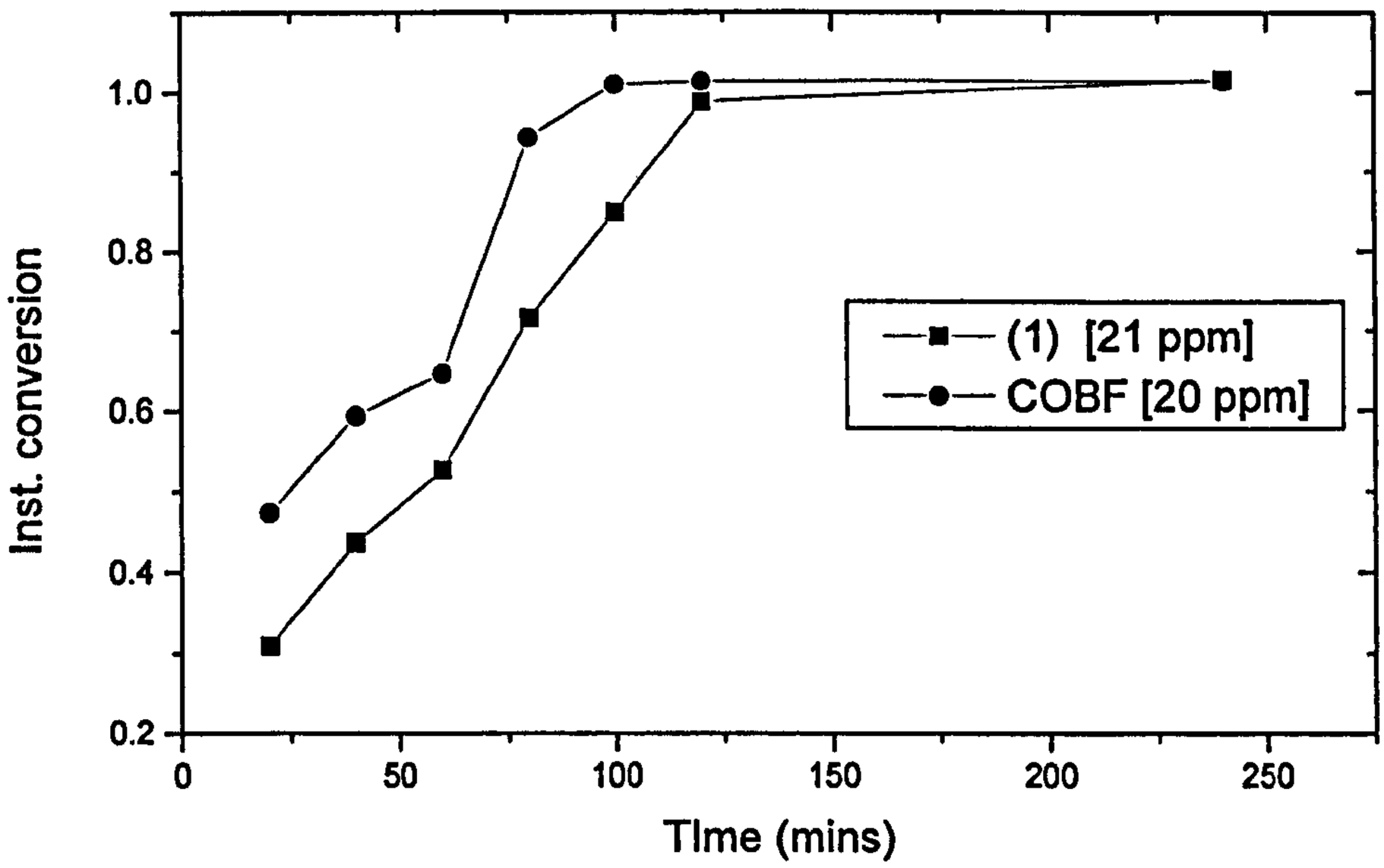


Figure 4.4 – *Instantaneous conversion versus time graph for polymerisations (1)*

The rate of reaction is slightly slower with the polymerisation employing catalyst (1) as a transfer agent than for the COBF agent which is consistent with more of

the transfer agent being present at the locus of polymerisation for the more MMA soluble catalyst (1) and lower molecular weight polymer being formed.

Catalyst (2)

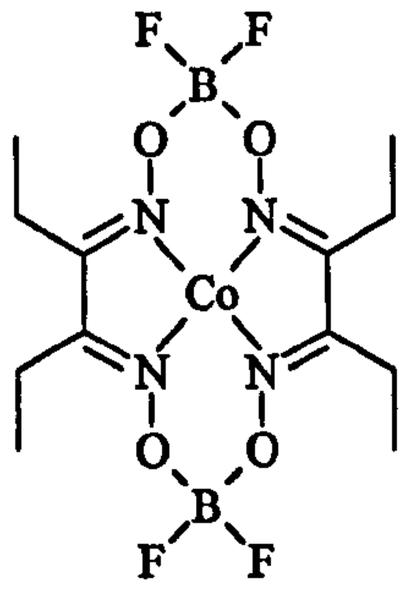


Figure 4.5 – *Structure of Catalyst (2)*

Reaction	Wt. COBF (g)	Ppm COBF	Feed Conditions	Mn	PDI	Inst. Conv.	Cs^E
(2) a	0.0155	16.41	100% fed	1790	1.48	0.915	3406
(2) b	0.034	35.48	100% fed	789	1.41	0.527	3576

Table 4.2 – *End conditions of emulsion polymerisations (2)a and (2)b*

On increasing the size of the catalytic chain transfer agent to that shown in figure 4.5 the molecular weight is again decreased more than for the equivalent concentration of the COBF catalyst. By comparing the Cs^E values of the two catalysts it can be seen that catalyst (2) is over three times more effective at reducing the molecular weight of MMA polymers in emulsion than the COBF transfer agent and also one and a half times more effective than catalyst (1).

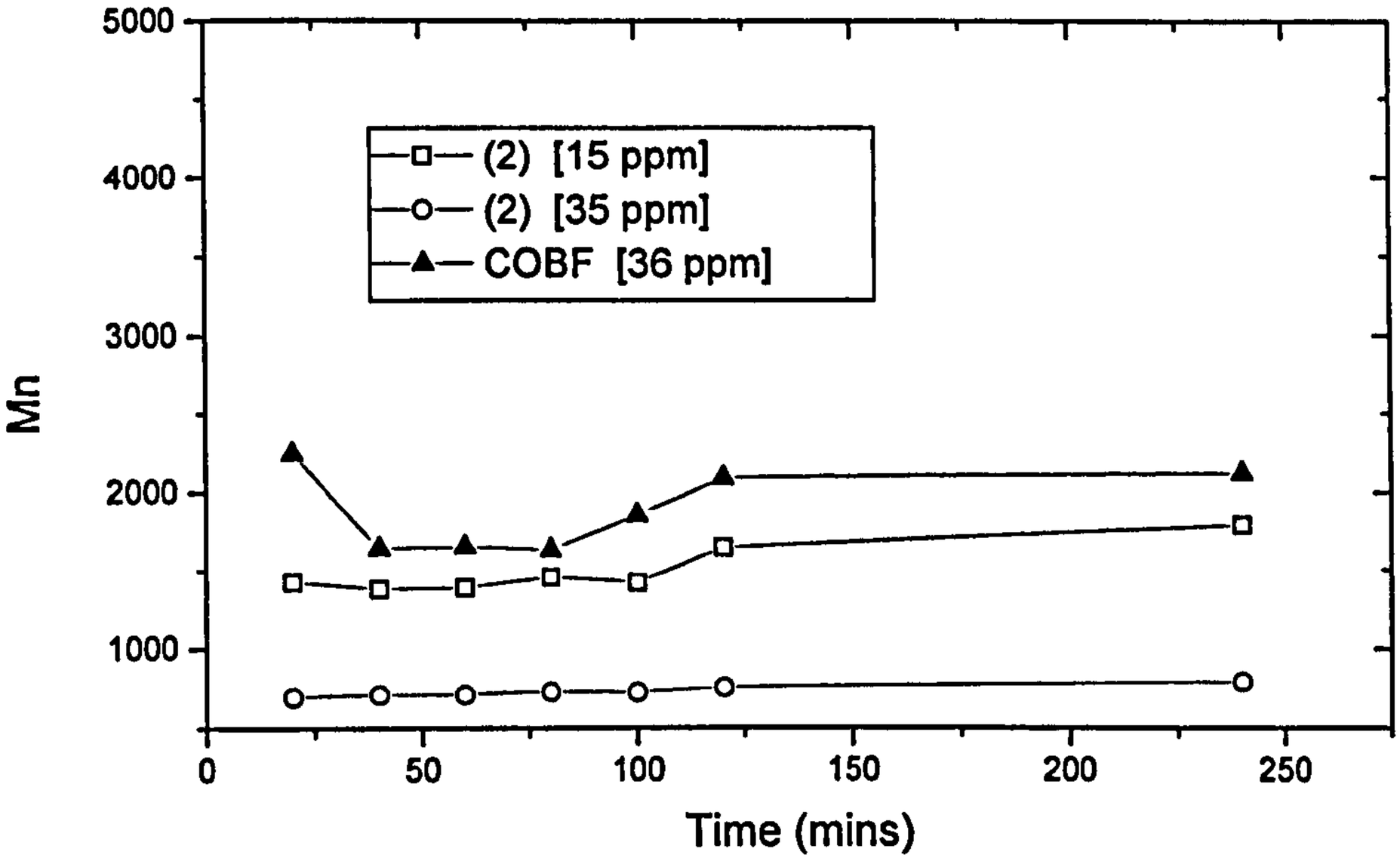


Figure 4.6 - *M_n versus time graph for emulsion polymerisations (2)a and (2)b*

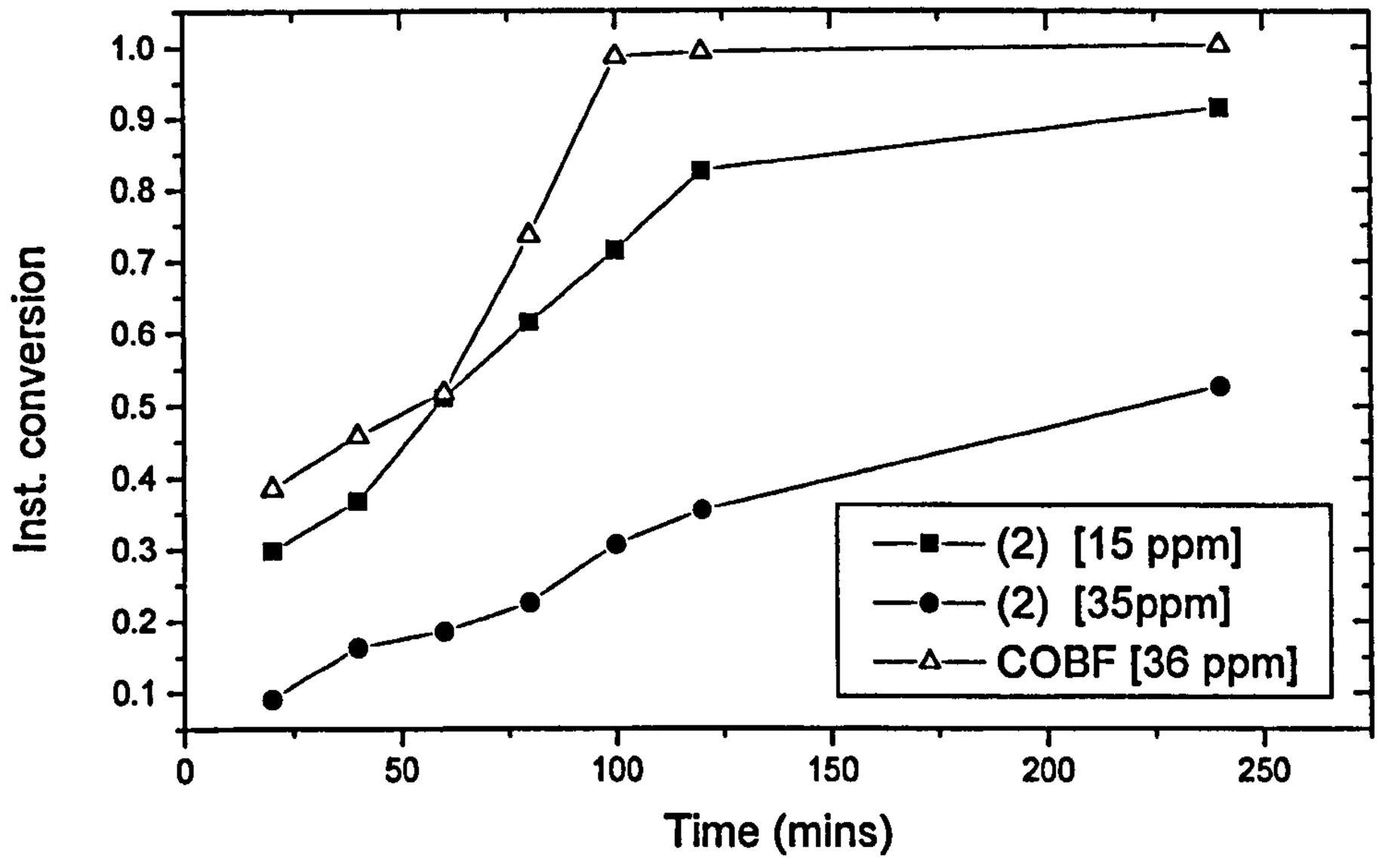


Figure 4.7 - *Instantaneous conversion versus time graph for emulsion polymerisation (2)a and (2)b*

The M_n versus time graph shown in figure 4.6 shows how effective catalyst (2) is at reducing molecular weight. The partitioning of catalyst (2) and transfer constant in MMA at 60 °C have been measured as $[(2)]_{MMA} / [(2)]_{aq} = 99.0$ and 14 000 respectively[9]. It can be seen from the partitioning data that almost all of the catalyst added to the system is available for the CCT reaction resulting in the high observed transfer constant in emulsion.

Catalyst (2) has been shown to be much more effective at molecular weight reduction than COBF, but if the rate of reaction is observed in figure 4.7 it can be seen that the rate of reaction is very much slower than for the standard COBF transfer agent. Also it can be seen that the level of catalyst used in the reaction has a very large effect on the rate of polymerisation, when the catalyst concentration is doubled there is a dramatic increase in the time taken to reach 100% conversion. For the 15 ppm level of catalyst the reaction is completed after 4 hours but for the 36 ppm catalyst level polymerisation after the same amount of time the reaction has only reached 52% conversion. The result of this is that although the Cs^E value is much higher for catalyst (2) this is achieved at the expense of reaction time. This result has implications for the industrial application of such catalysts since although there is the reduction in cost by the fact that less catalyst needs to be employed, the extra reaction time will add considerable expense to the reaction making the use of catalyst (2) unfavourable.

Catalyst (3)

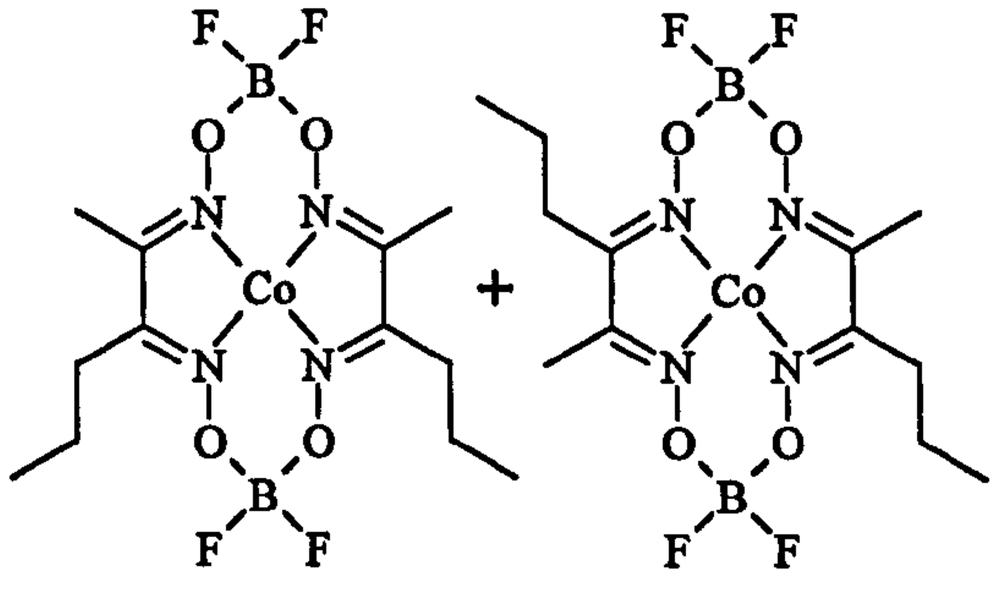


Figure 4.8 – *Structure of Catalyst (3)*

Reaction	Wt. COBF (g)	Ppm COBF	Feed Conditions	Mn	PDi	Inst. Conv.	Cs^E
(3)	0.0294	25.48	100% fed	20700	1.77	1.023	189

Table 4.3 – *End properties of emulsion polymerisation (3)*

Catalyst (4)

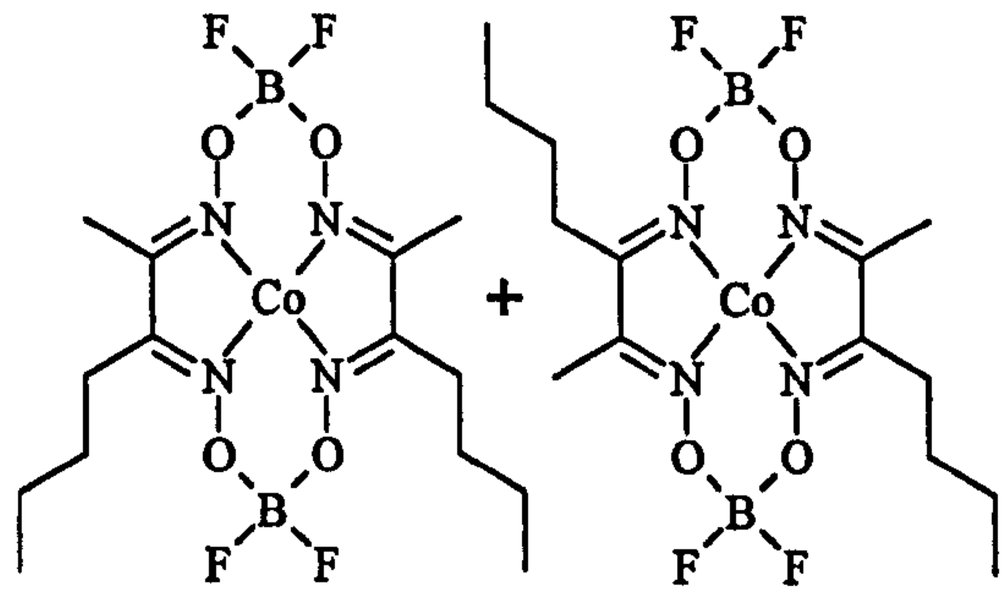


Figure 4.9 – *Structure of Catalyst (4)*

Reaction	Wt. COBF (g)	Ppm COBF	Feed Conditions	Mn	PDi	Inst. Conv.	Cs^E
(4)	0.0305	25.285	100% fed	29200	1.90	1.044	135

Table 4.4 – *End properties for emulsion polymerisation (4)*

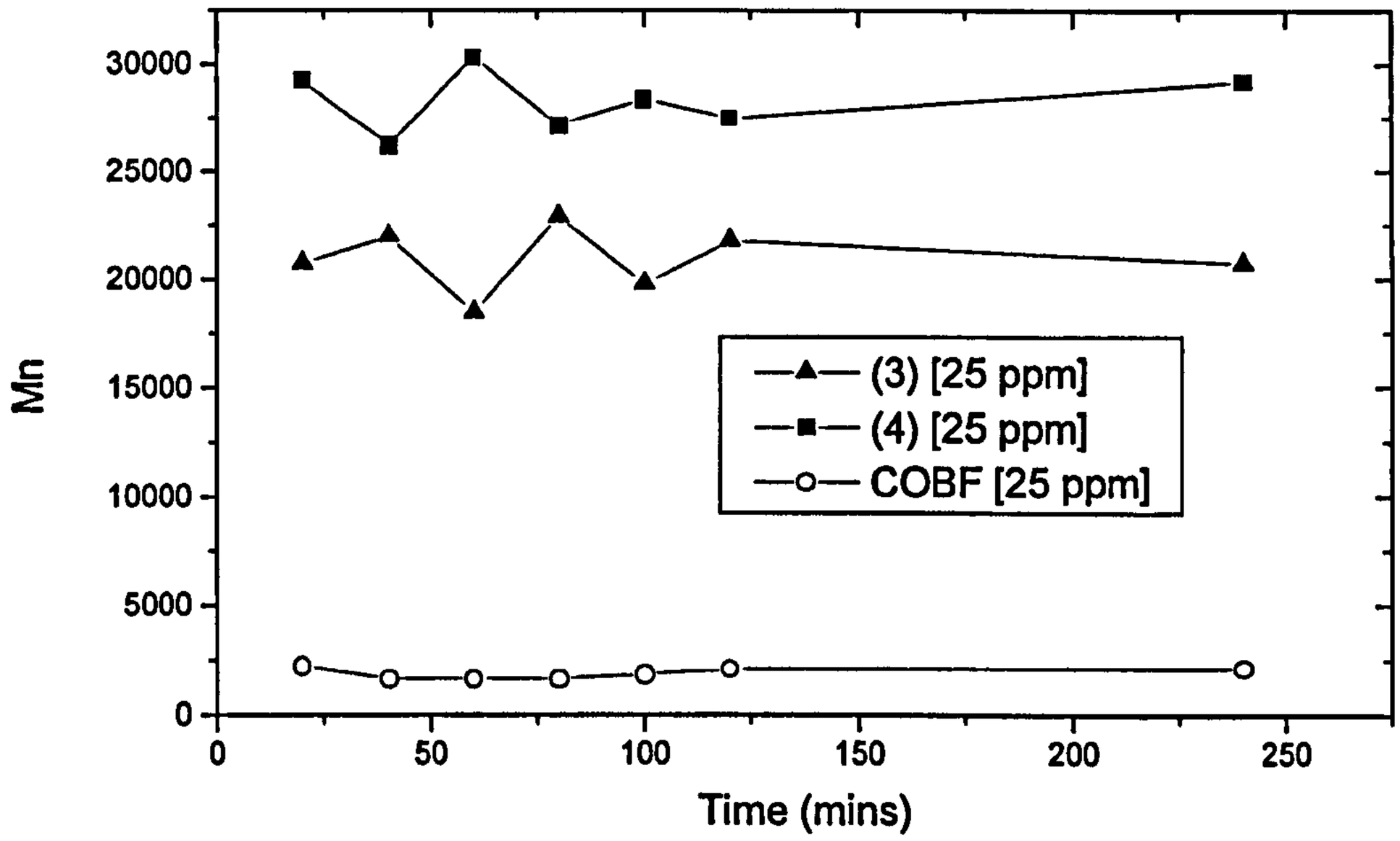


Figure 4.10 – *M_n versus time graph for polymerisations (3) and (4)*

It can be seen in figure 4.10 that both catalysts (3) and (4) both do not give as effective molecular weight reductions as COBF for the CCT emulsion polymerisations of MMA. The final molecular weights for the polymerisations involving catalysts (3) and (4) are considerably higher than for the equivalent COBF reaction. As the polymerisations progressed for catalysts (3) and (4) it was observed that CCT agent was depositing itself on the inside of the reaction vessel. The water solubilty of these catalyst is negligible and the transfer of

catalyst between particles and from monomer droplets to the particles would not occur readily. As the emulsion polymerisation progressed from interval II to interval III (see chapter 1) the monomer droplets will disappear and since the catalyst is dissolved in the droplets, when the droplets disappear if the catalyst cannot transfer to particles through the aqueous phase, the catalyst will precipitate out of the water. The precipitation of the catalyst will lead to a low effective concentration at the locus of polymerisation in the particles and hence a low Cs^E value is observed.

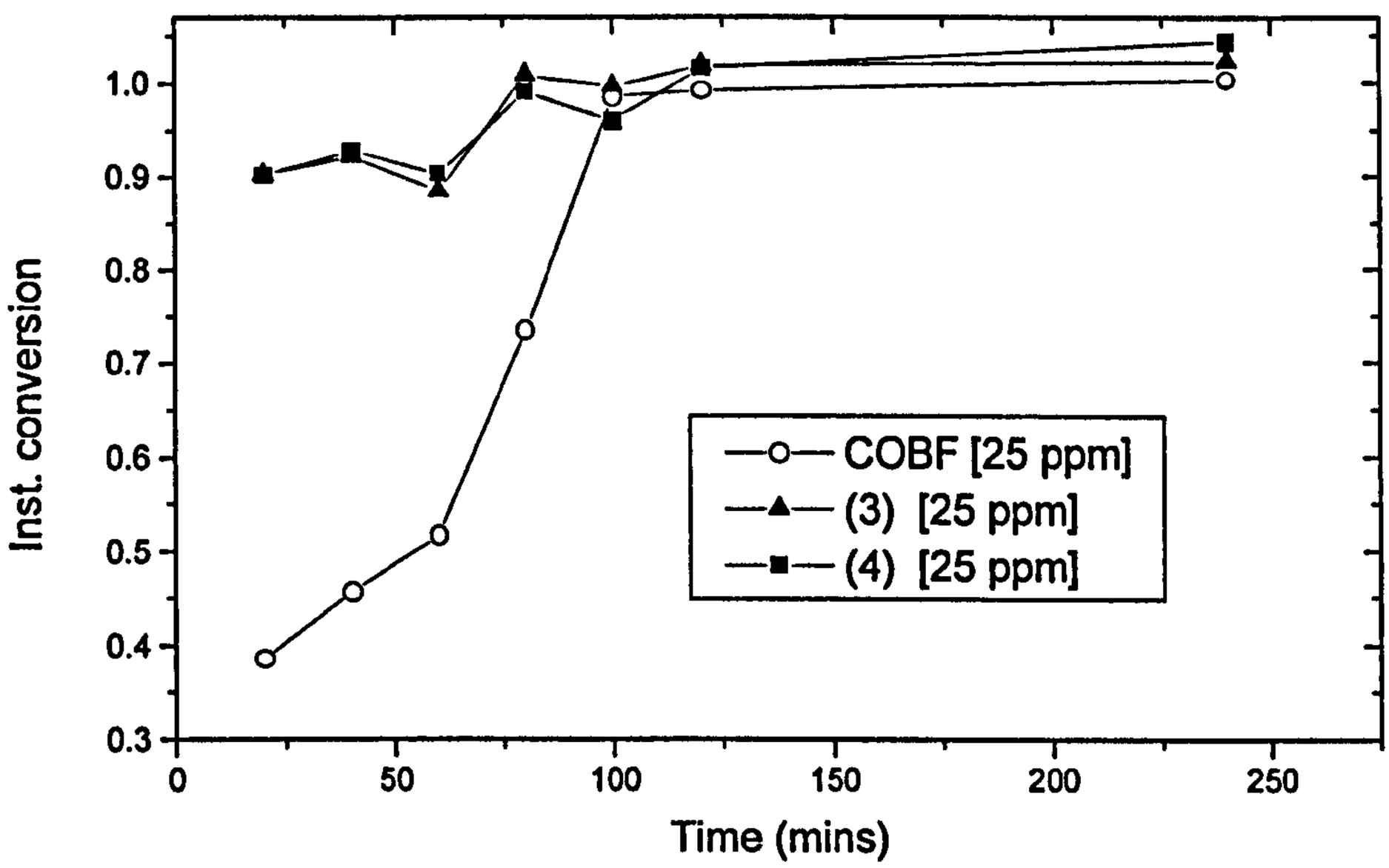


Figure 4.11 - *Instantaneous conversion versus time graoh for polymerisations (3) and (4)*

A low concentration of catalyst is present in the particles for emulsion polymerisations (3) and (4) and so it can be observed that the reaction is operating under non – starved fed conditions as observed for an MMA emulsion polymerisation with no catalyst present, this is shown in figure 4.11.

Catalyst (5)

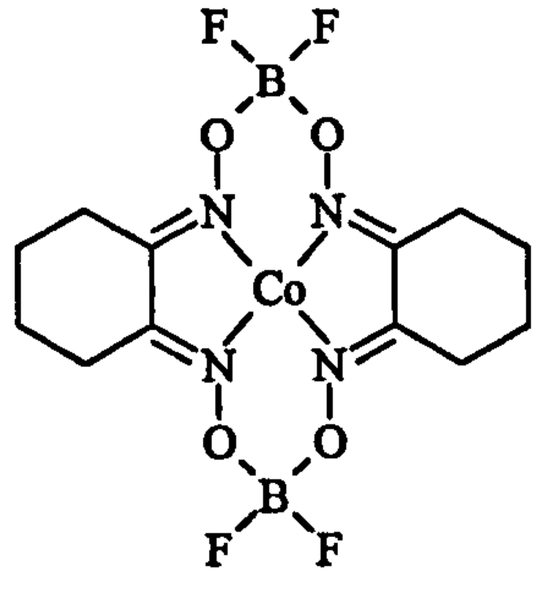


Figure 4.12 – *Structure of Catalyst (5)*

Reaction	Wt. COBF (g)	Ppm COBF	Feed Conditions	Mn	PDi	Inst. Conv.	Cs^E
(5) a	0.0301	32.14	100% fed	1730	2.23	0.902	1801
(5) b	0.015	16.02	100% fed	3760	1.81	1.022	1664
(5) c	0.0106	11.32	100% fed	4990	1.84	1.022	1774

Table 4.5 – *End properties for emulsion polymerisations (5)a, (5)b and (5)c*

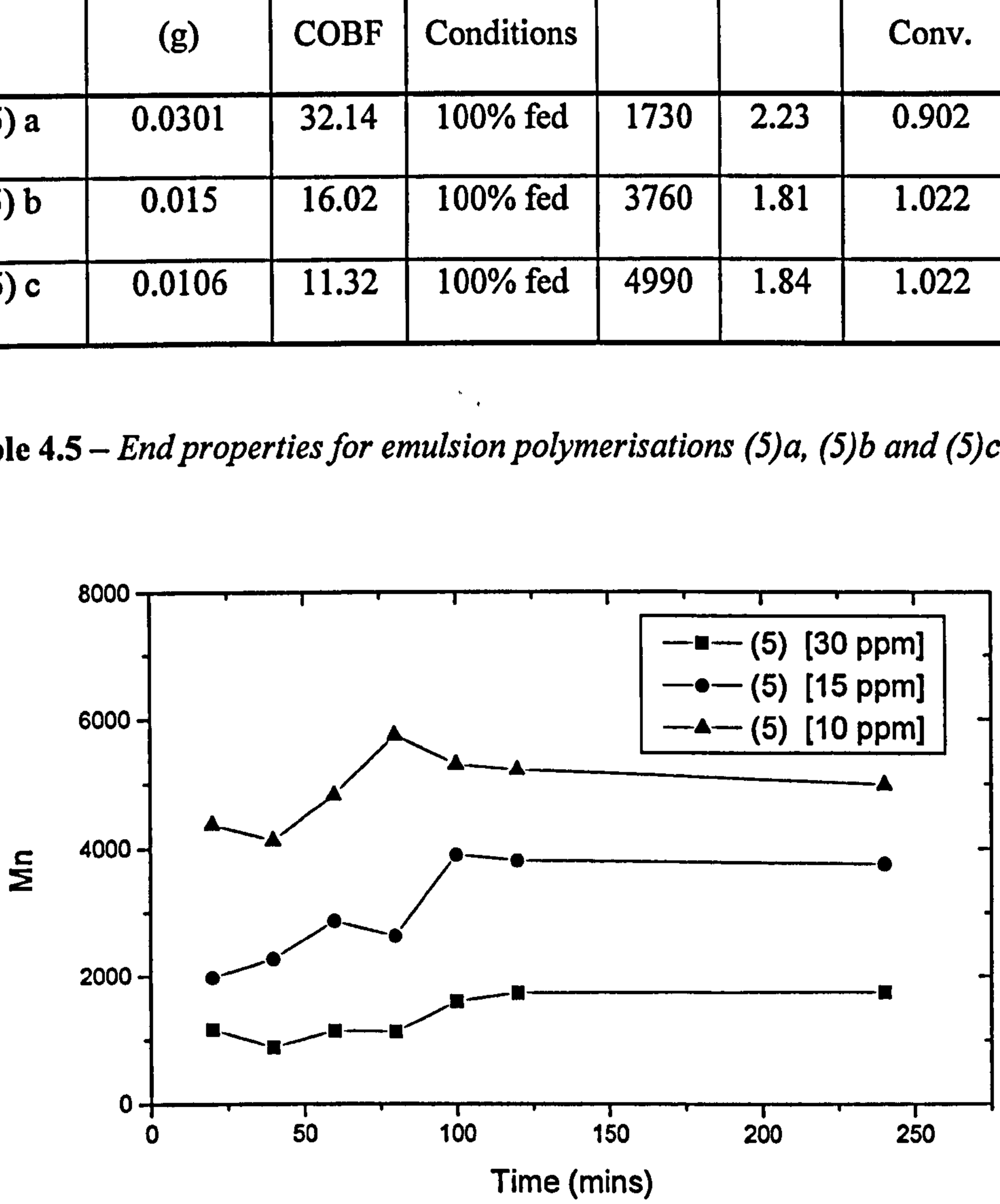


Figure 4.13 – *M_n versus time graph for polymerisations (5)a, (5)b and (5)c*

It can be seen in figure 4.13 that the molecular weight of the polymers made with catalyst (5) added as a transfer agent have been reduced successfully. The molecular weights for these polymers are lower than the equivalent reaction with the same concentration of COBF catalyst and so this catalyst has a higher Cs^E value than the COBF. When the *pseudo* Mayo plot is drawn for this set of reactions (figure 4.14) the Cs^E value is calculated as 1848 which higher than that measured for COBF.

At 60 °C the chain transfer constant for this catalyst in the bulk polymerisation of MMA has been measured at nearly 14 000 [10] which is under half the transfer constant for the CCT agent COBF under identical conditions.
The catalyst is more soluble in MMA than COBF and this results in a higher observed transfer constant in the emulsion polymerisation of MMA than for COBF.

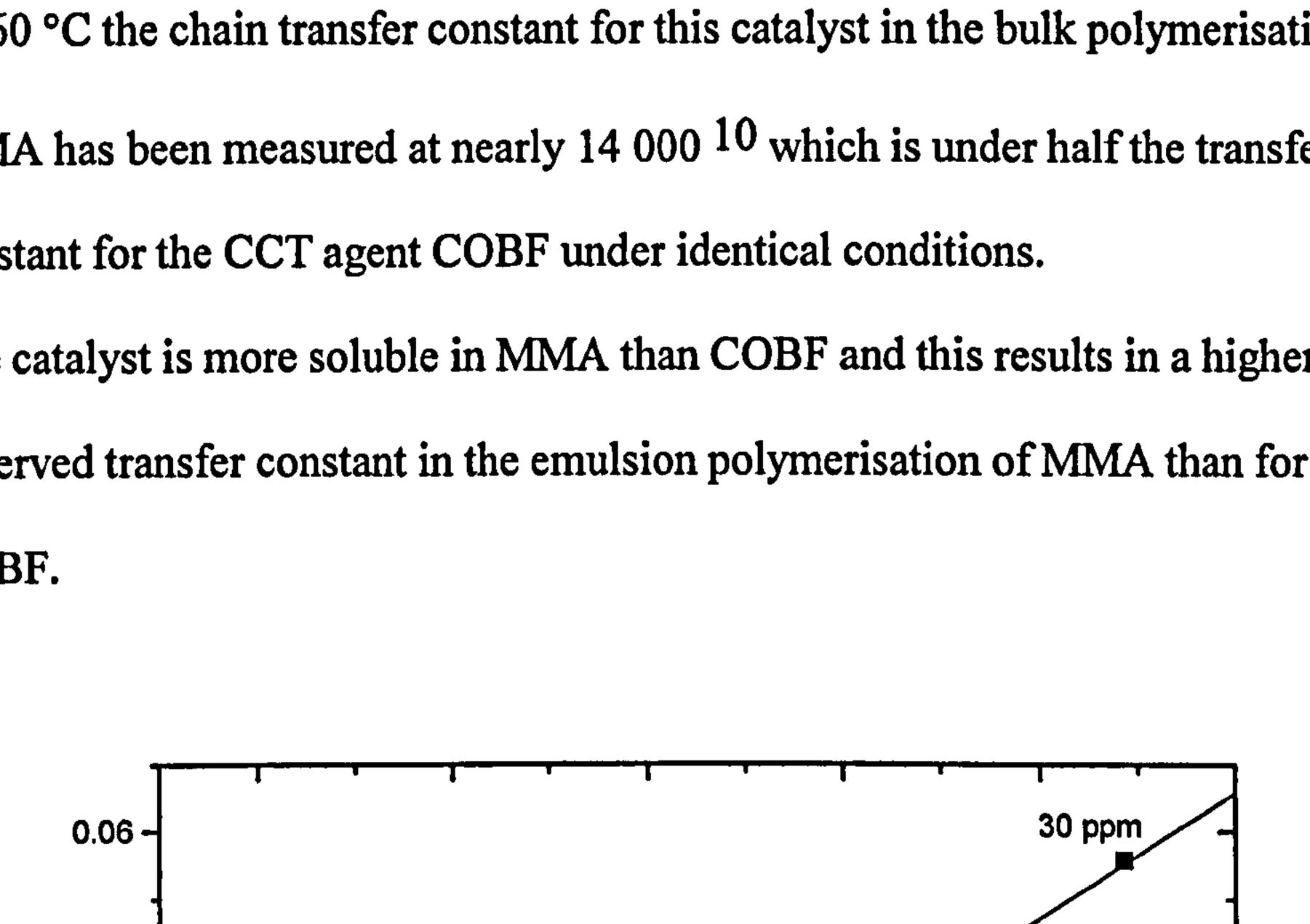


Figure 4.14 – *Pseudo Mayo plot for catalyst (5)*

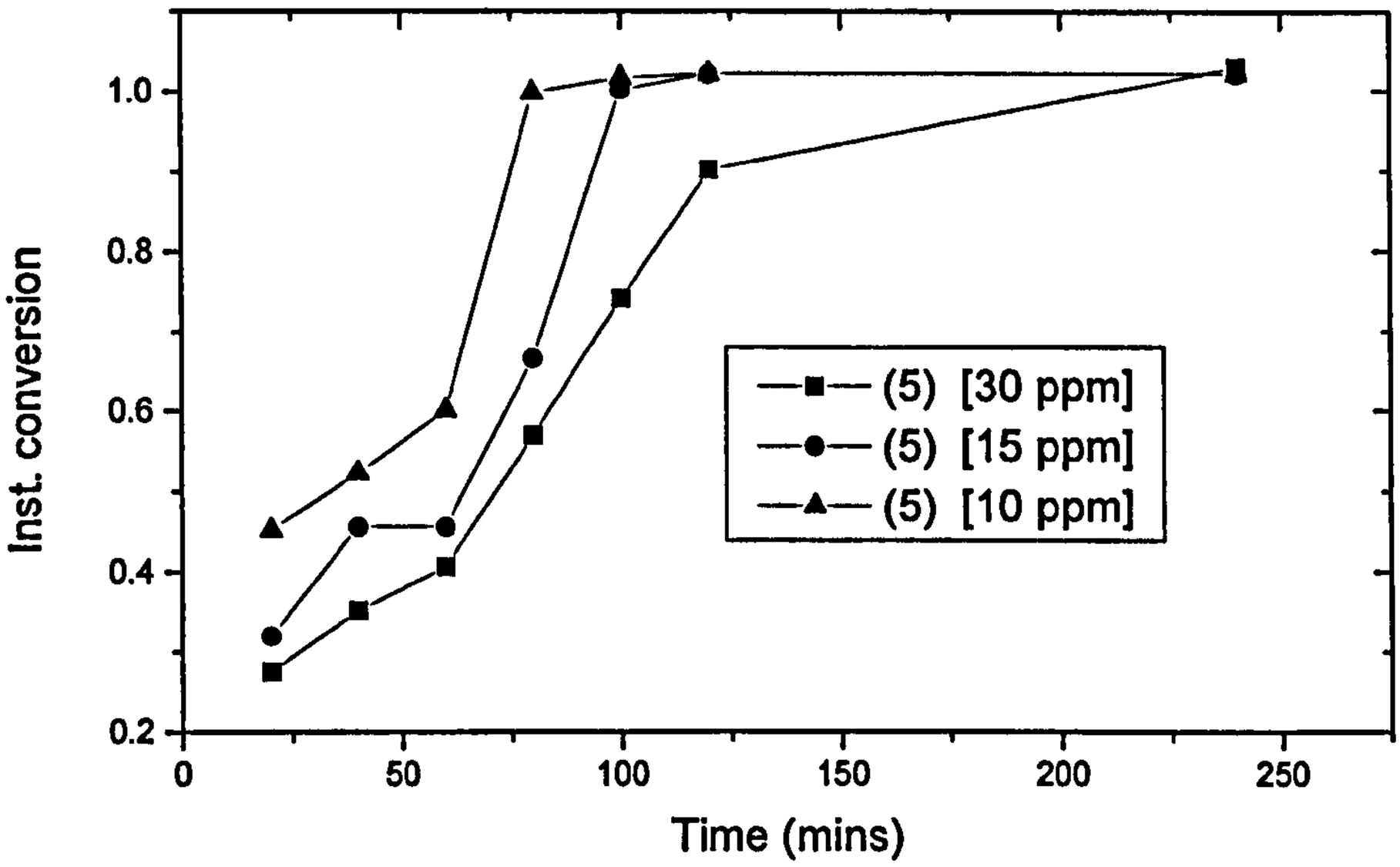


Figure 4.15 – *Instantaneous conversion versus time graph for polymerisations (5)a, (5)b and (5)c*

The rate of polymerisation can be seen to vary with concentration of catalyst as expected. The higher the amount of catalyst in the system the slower the rate of polymerisation. The rate of polymerisation can also seen to be slightly slower than for the equivalent COBF polymerisation. This observation is consistent with higher concentration of catalyst at the locus of polymerisation and hence lower molecular weight polymer being synthesised.

Catalyst (6)

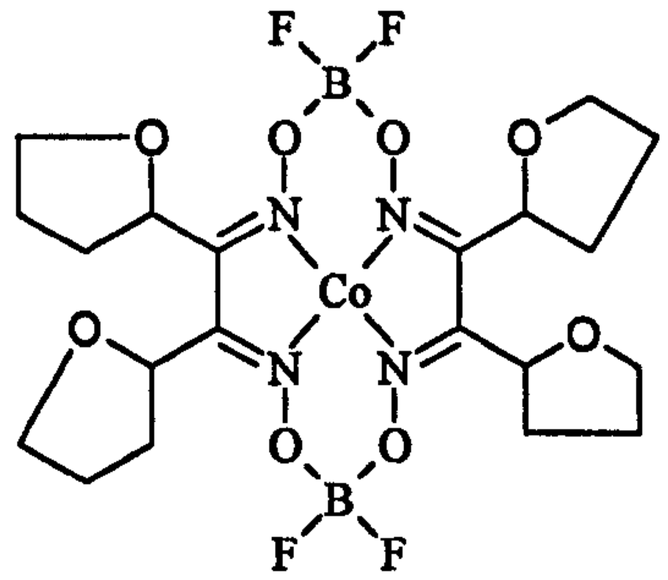


Figure 4.16 – *Structure of Catalyst (6) (mixture of isomers)*

Reaction	Wt. COBF (g)	Ppm COBF	Feed Conditions	Mn	PDi	Inst. Conv.	Cs^E
(6)	0.0294	23.36	100% fed	53300	1.98	1.003	80

Table 4.6 – *End properties for emulsion polymerisation (6)*

It was found that by increasing the bulkiness of the catalyst to that of catalyst (6) that there was a large decrease in observed transfer constant in emulsion. The molecular weight data is shown in figure 4.17 and it shows that catalyst (6) is not very effective at reducing the molecular weight of MMA polymers. The observed transfer constant for this catalyst is considerably lower than for COBF transfer agent with the Cs^E value being under a tenth of that for COBF.

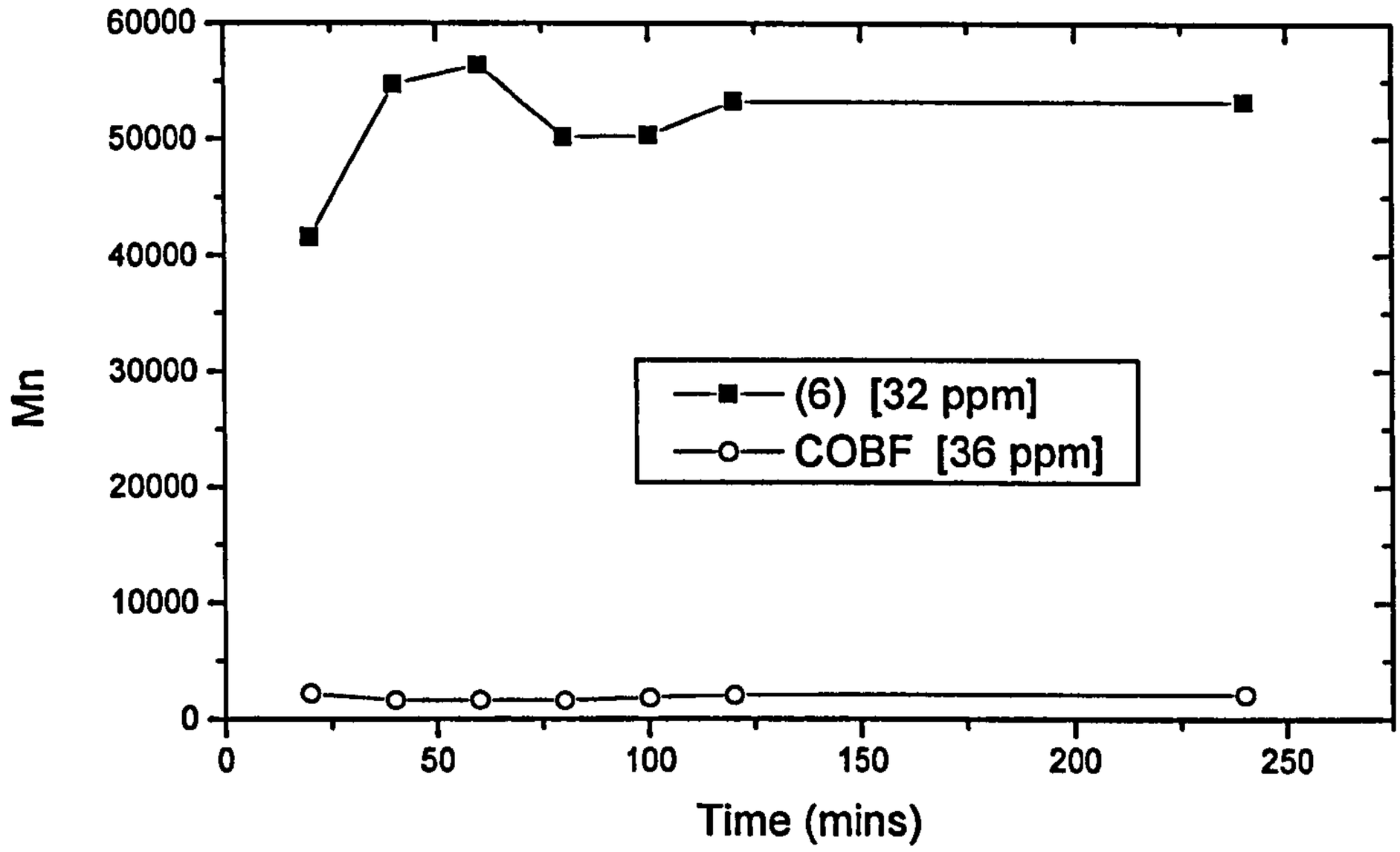


Figure 4.17 – *M_n versus time graph for polymerisations (6)*

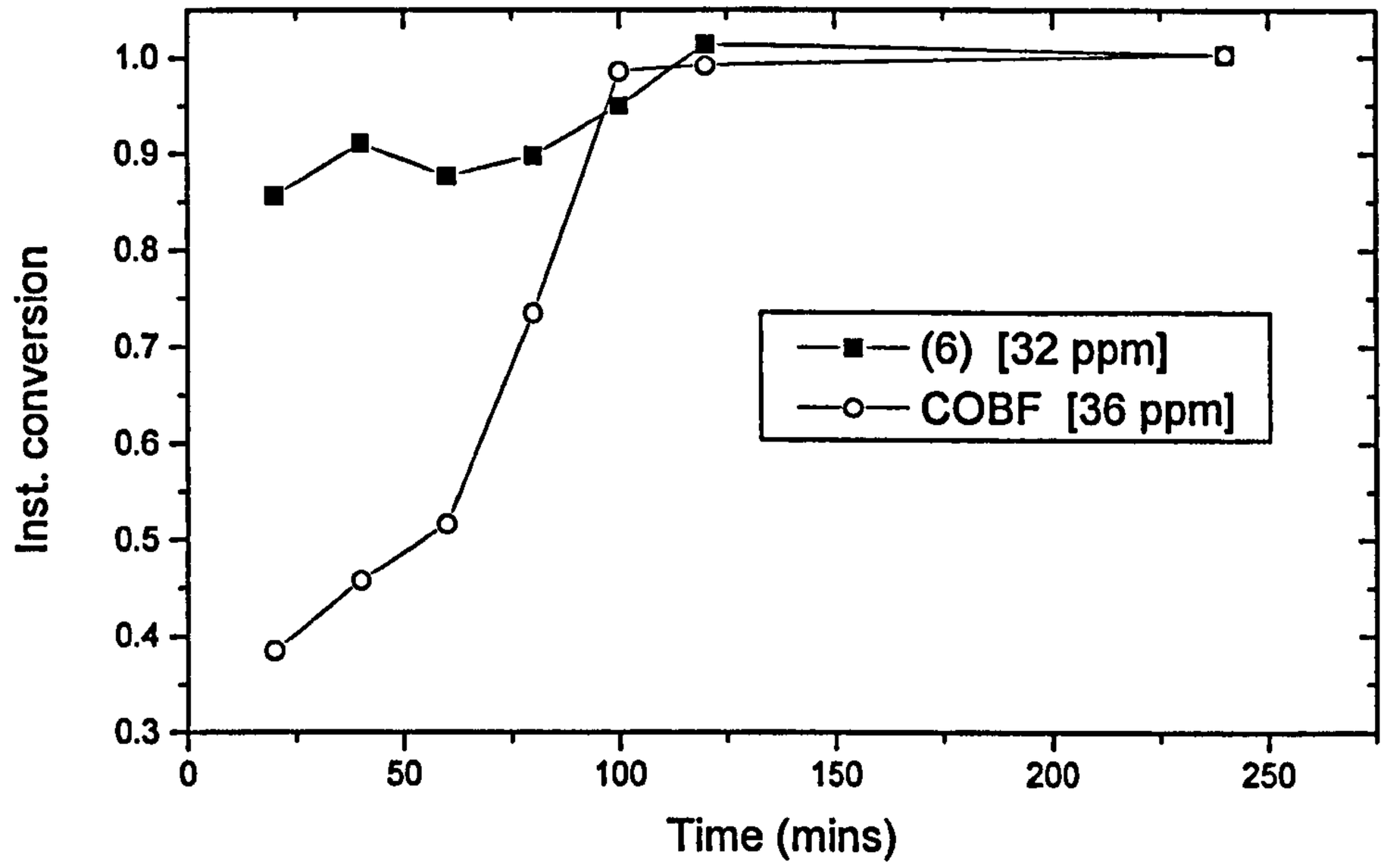


Figure 4.18 – *Instantaneous conversion versus time graph for polymerisation (6)*

The rate of polymerisation is much faster than for the reaction where effective CCT is observed. The catalyst is too soluble in the MMA droplets and cannot transport across the aqueous phase to the particles resulting in the very low observed Cs^E value.

Catalyst (7)

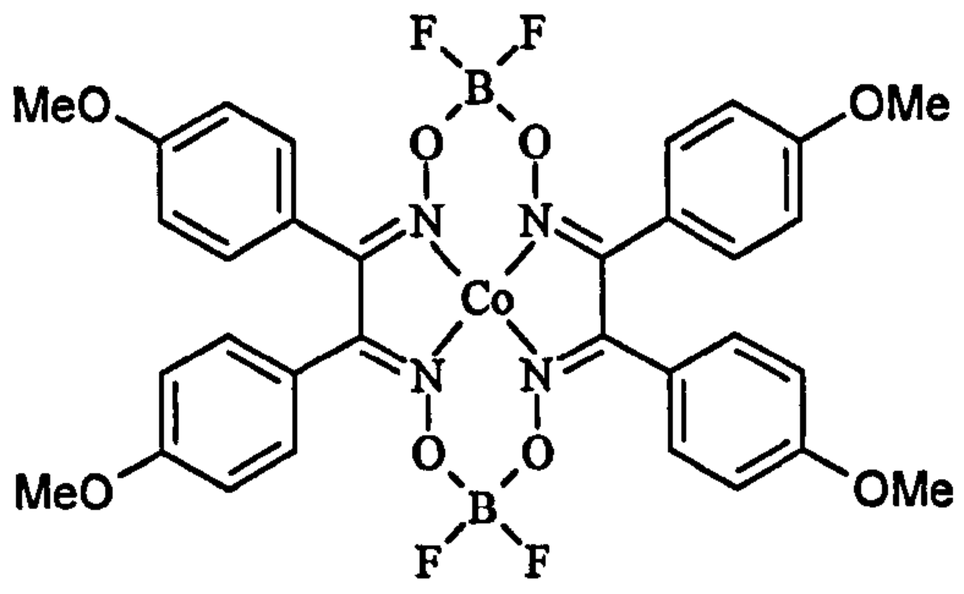


Figure 4.19 – *Structure of Catalyst (7)*

Reaction	Wt. COBF (g)	Ppm COBF	Feed Conditions	Mn	PDi	Inst. Conv.	Cs^E
(7) a	0.0395	25.85	100% fed	11300	1.56	0.979	344
(7) b	0.0286	18.71	100% fed	17300	1.65	0.990	309
(7) c	0.0109	23.77	100% fed	29800	1.62	0.995	141

Table 4.6 – *End properties for emulsion polymerisations (7)a, (7)b and (7)c*

Chain transfer agent (7) is a functionalised version of CoPhBF (see section 1.7.1) which does not give efficient transfer activity in emulsion. The reason the CoPhBF catalyst had such a low transfer constant was the almost complete insolubility of the catalyst in the water phase. Catalyst (7) has methoxy groups

on the phenyl rings and polymerisations were carried out to see if these have the effect of making the catalyst more soluble in the water phase.

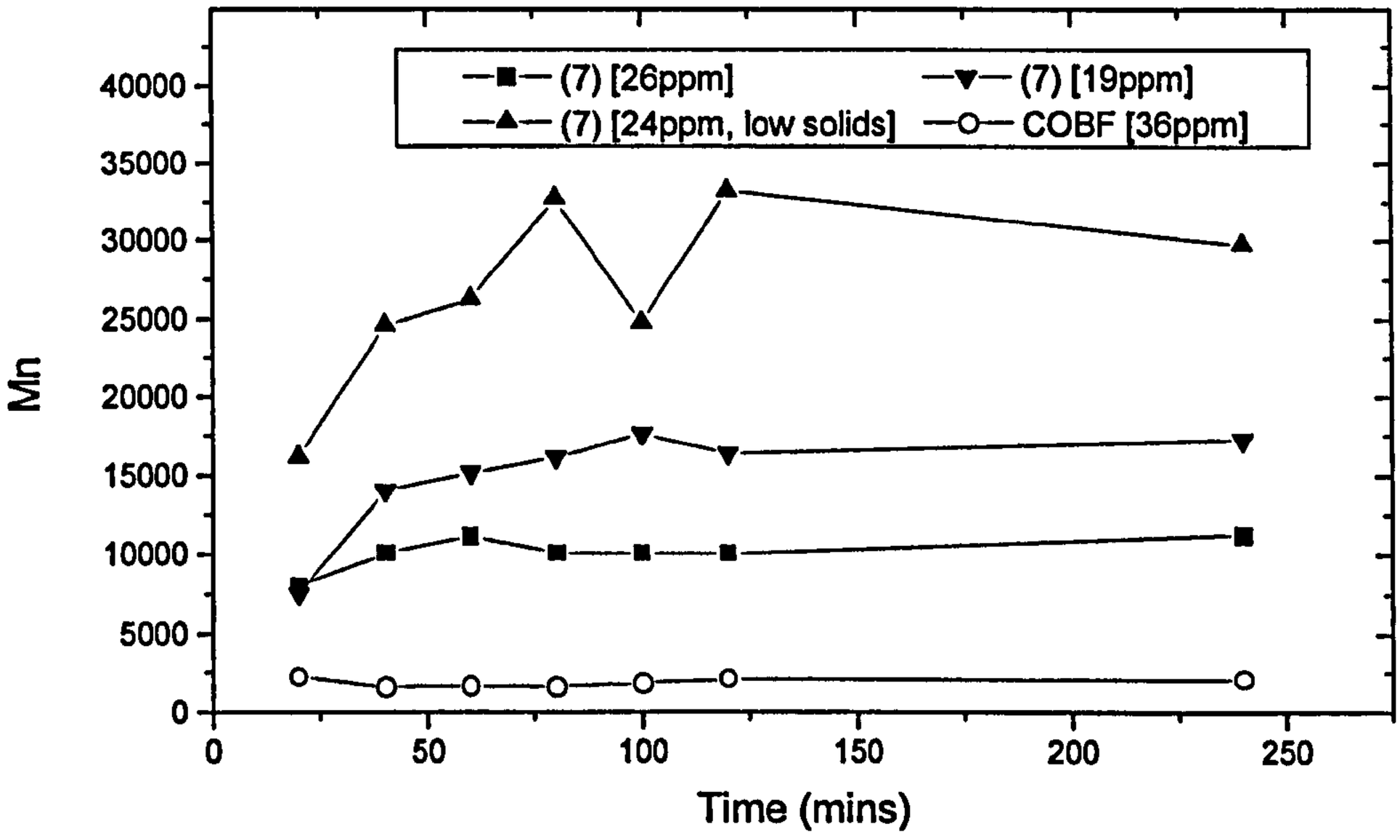


Figure 4.20 – *M_n versus time graph for polymerisations (7)a, (7)b and (7)c*

As shown for other low water soluble catalysts in this section, catalyst (7) is not as effective at reducing the molecular weight of MMA polymers as COBF. The transfer constant is under a quarter of the value for the COBF transfer agent again due to the fact that the water solubility is too low to allow effective CCT in emulsion. A low solids emulsion was attempted to see if this had any effect on the transfer constant for the reaction. For the low solids reaction instead of the usual recipe of 200 mL of monomer and 450 mL of water only 60 mL of monomer was used with the same amount of water. The resulting latex from this reaction would only be approximately 10% solids instead of the usual 30%. The transfer constant for the low solids polymerisation is lower than for the higher solids reaction. The catalyst must be slightly soluble in the water phase so when

the amount of water is increased, the concentration of the catalyst in the particles decreases, lowering the Cs^E .

The instantaneous conversion versus time plots for these emulsion polymerisations are shown in figure 4.21. A faster rate of polymerisation is observed when catalyst (7) is used as the catalytic chain transfer agent compared to when COBF is used. The low concentration of catalyst in the particles has resulted in ineffective CCT in emulsion and the higher rate of polymerisation.

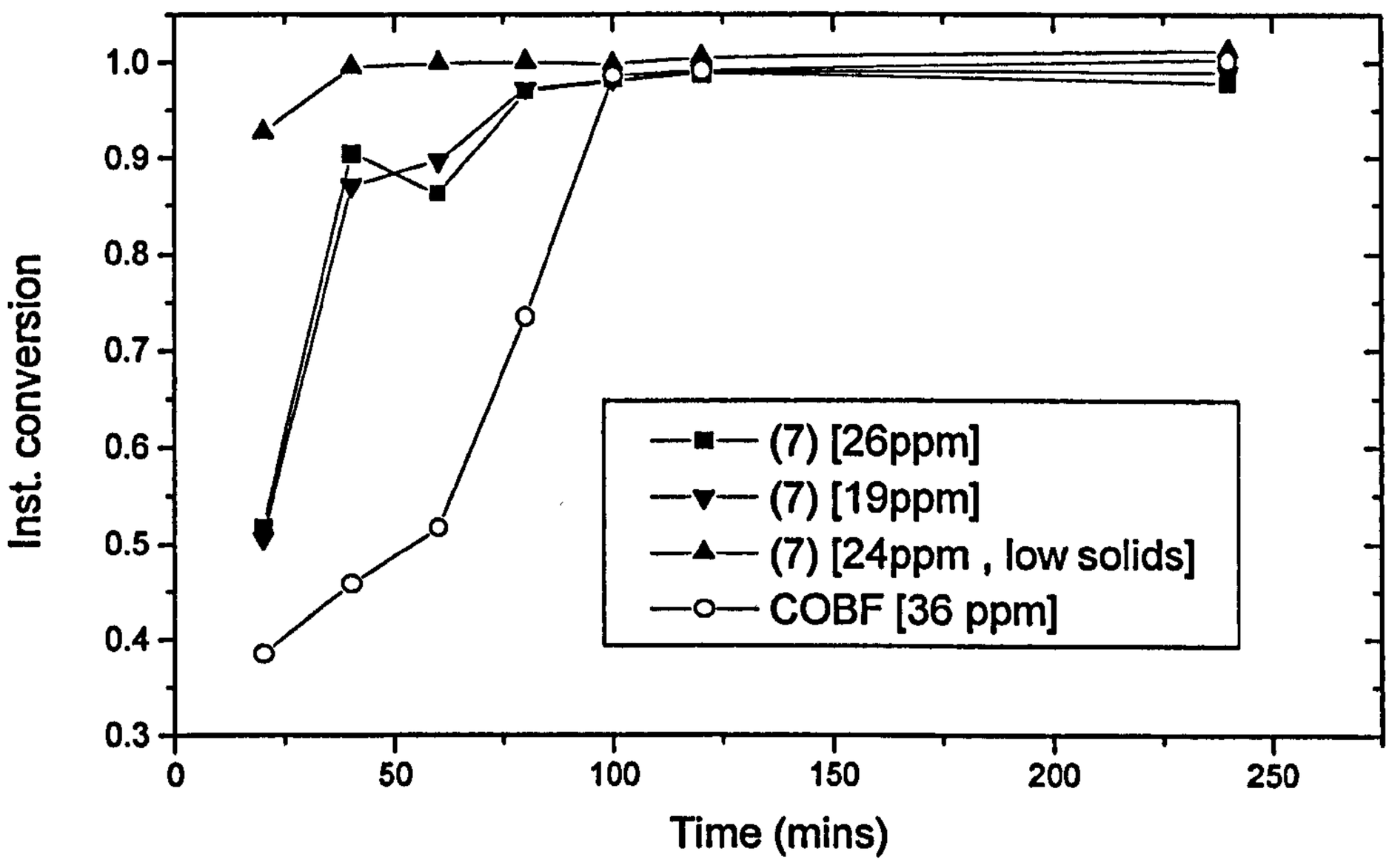
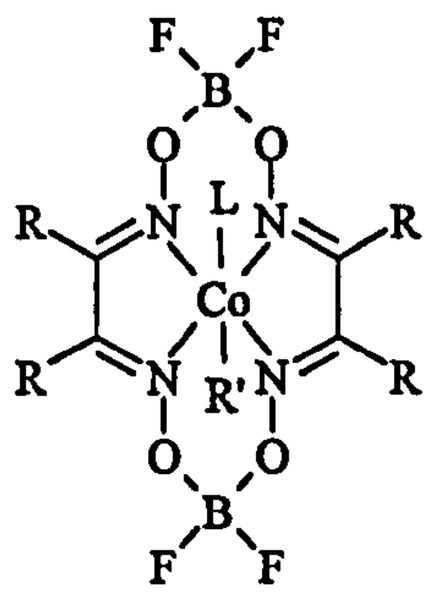


Figure 4.21 – *Instantaneous conversion versus time graph for polymerisations (7)a, (7)b and (7)c*

4.3 Co(III) Catalysts

It has been shown previously[11-13] that cobalt (III) complexes may be used as catalytic chain transfer agents and are useful in reducing the molecular weight in

the polymerisation of methyl methacrylate (see section 1.7) . Catalysts of the general structure shown in figure 4.22 can be used as transfer agents. The Co(III) catalysts are thought to operate as CCT agents by the homolysis of the cobalt – alkyl bond yielding a cobalt (II) species that can perform the CCT reactions.



L = 2 electron donating ligand
e.g. methanol

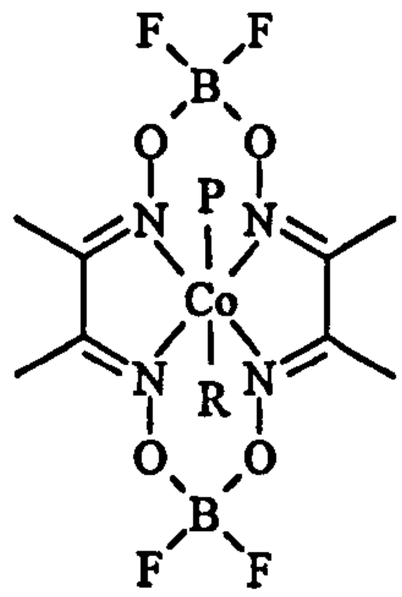
R = alkyl group

R' = 1 electron donating ligand
e.g. ethyl group

Figure 4.22 – *General structure of Co(III) CCT agents*

The synthesis of cobalt (III) complexes have certain advantages over their Co(II) counterparts, namely the increased stability of the catalyst and the fact that it is possible to analyse the complexes by NMR allowing the simple characterisation of such complexes.

Catalyst (8)



P = Pyridine
R = Ethyl

Figure 4.23 – *Structure of Catalyst (8)*

Reaction	Wt. COBF (g)	Ppm COBF	Feed Conditions	Mn	PDI	Inst. Conv.	Cs^E
(8)	0.0291	31.44	100% fed	11900	2.83	1.025	268

Table 4.7 – *End properties of emulsion polymerisation (8)*

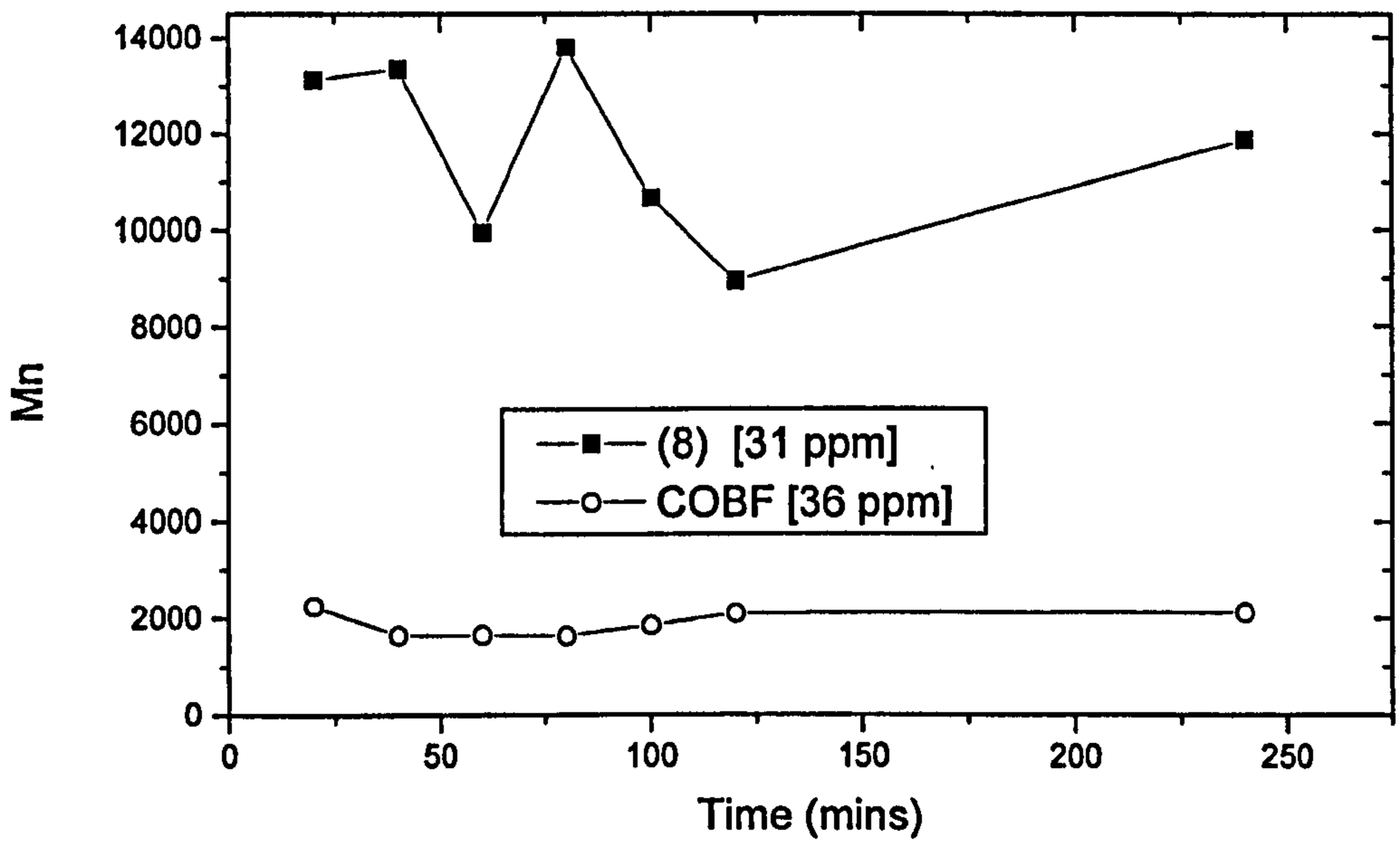


Figure 4.24 – *M_n versus time graph for polymerisation (8)*

The graph shown in figure 4.24 compares the molecular weight as a function of time for the emulsion polymerisation of MMA using COBF as the CCT agent with a polymerisation using the equivalent Co (III) complex. The reactions employ similar concentrations of catalyst based on moles of catalyst : moles of monomer. It can be seen that the molecular weight reduction for the Co (III) complex is much less that for the Co (II) complex. Comparing the Cs^E values for the reaction it can be seen that the Co (III) complex is less than a quarter as

effective at reducing the molecular weight of MMA polymers in emulsion polymerisation as the Co (II) complex.

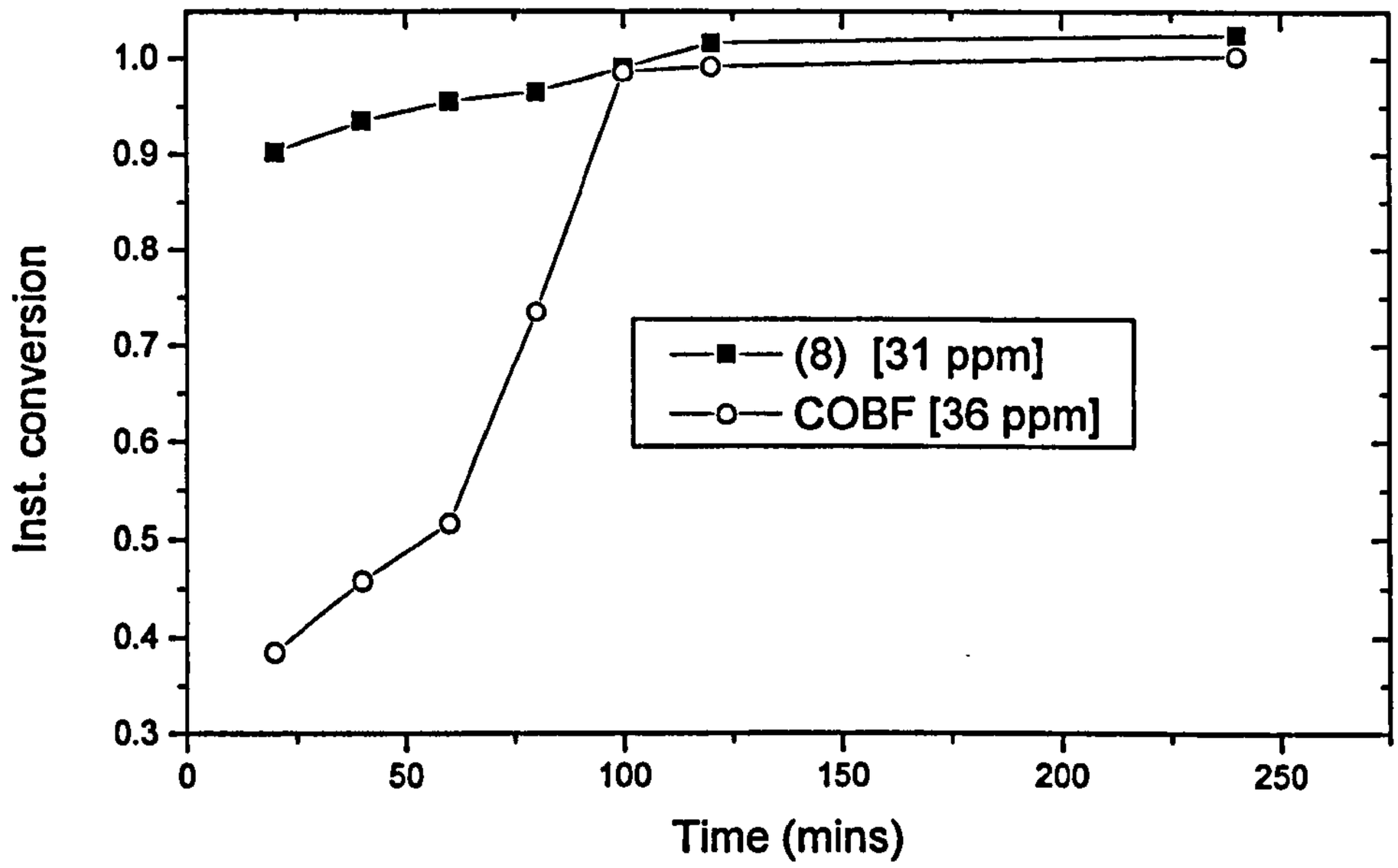


Figure 4.25 – *Instantaneous conversion versus time graph for polymersation (8)*

If the rate of polymerisation is shown in figure 4.25 and it can be seen that the polymerisation involving Co (III) catalyst (8) is under starved fed conditions. The chain transfer constant (Cs) of catalyst (8) in the bulk polymerisation of MMA at 60°C is found to be ~17 000 and the catalyst partitions such that $[(8)]_{MMA} / [(8)]_{aq} = 13.3$ [9]. Although the majority of the catalyst is present in the monomer phase it is sufficiently soluble in the water phase to allow transport between the monomer droplets and the particles. These observations would suggest that this catalyst would be more effective at reducing molecular weight of MMA polymers in emulsion than the COBF but the Cs^E is quite low compared to the Co (II) species in contradiction with the bulk reactions and partitioning studies.

Catalyst (9)

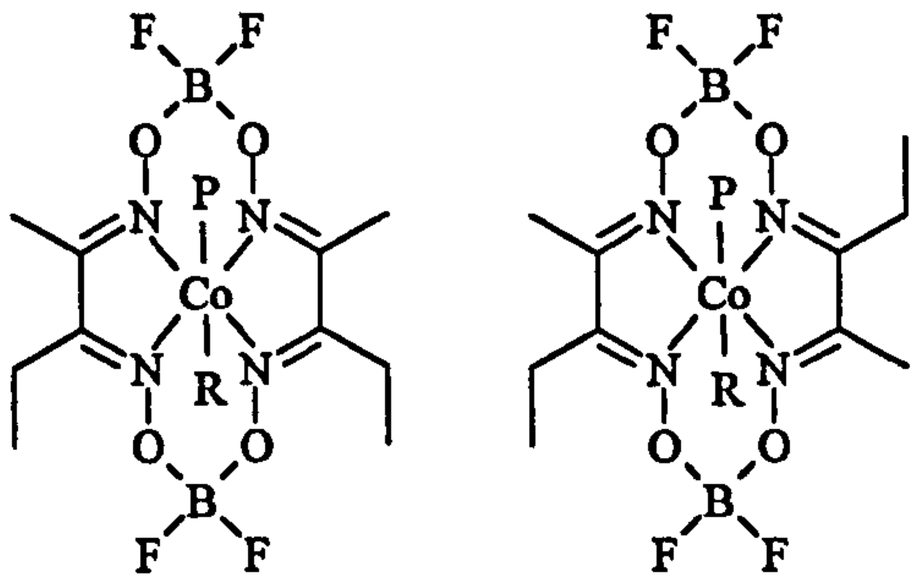


Figure 4.26 – *Structure of Catalyst (9)*

Reaction	Wt. COBF (g)	Ppm COBF	Feed Conditions	Mn	PDi	Inst. Conv.	Cs^E
(9)	0.0305	35.47	100% fed	3130	1.66	1.043	903

Table 4.8 – *End properties for emulsion polymerisation (9)*

The molecular weight data presented in figure 4.26 shows that the Co (III) version of CCT agent (1) (complex (9)), as for the cobalt (III) analogue of COBF, has a lower chain transfer constant in emulsion than the equivalent Co (II) complex.

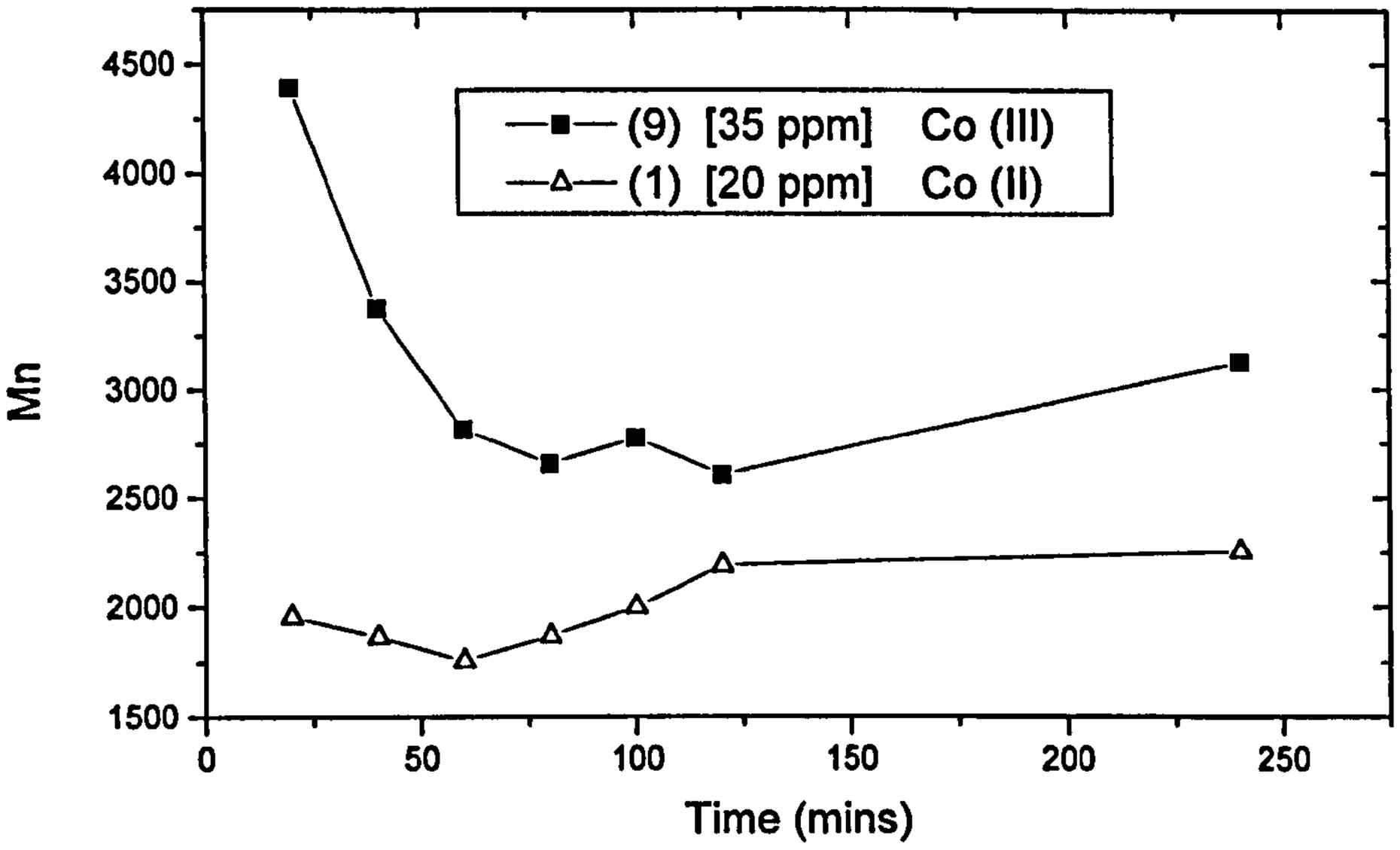


Figure 4.27 – *M_n versus time graph for polymersation (9)*

The observed chain transfer constant in emulsion of transfer agent (9) is approximately half that of its cobalt (II) analogue (900 compared to 2200). The Cs value in bulk at 60 °C is 4000 and partitioning results show that $[(9)]_{MMA} / [(9)]_{aq} = 49.0$. These results compare to a Cs of 12 300 and $[catalyst]_{MMA} / [catalyst]_{aq} = 8.09$ results for the Co (II) catalyst. It would be expected that the transfer constant in emulsion would be higher than for the Co (III) version but as for catalyst (8) the Cs^E is lower than would be predicted.

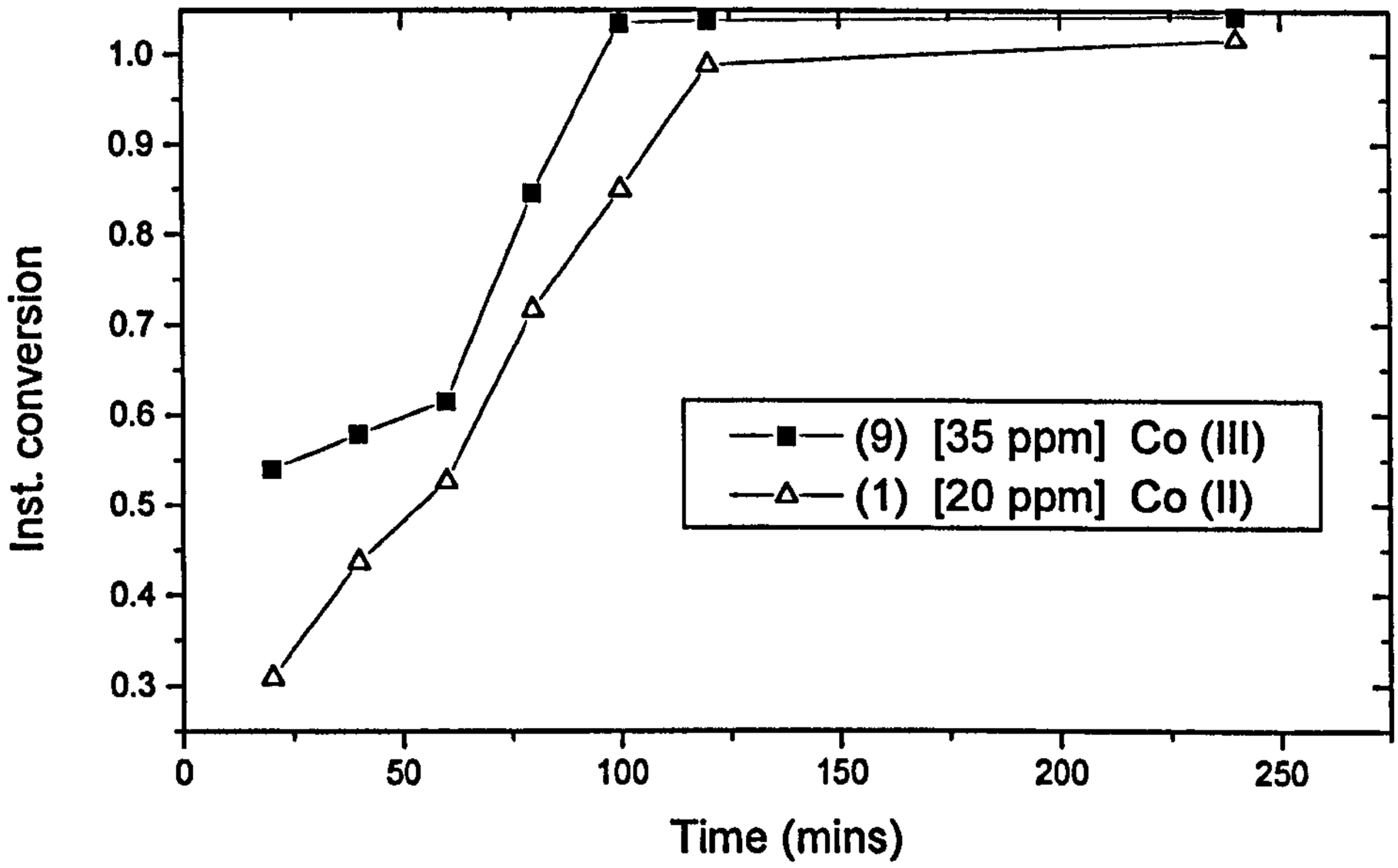
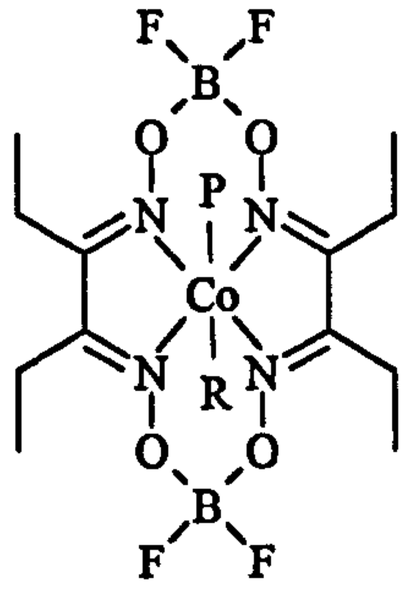


Figure 4.28 – *Instantaneous conversion versus time graph for polymerisation (9)*

Catalyst (10)



P = Pyridine
R = Ethyl

Figure 4.29 - *Catalyst (10)*

Reaction	Wt. COBF (g)	Ppm COBF	Feed Conditions	Mn	PDI	Inst. Conv.	Cs^E
(10) a	0.0248	24.11	100% fed	1780	1.55	1.009	2331
(10) b	0.0175	17.02	100% fed	2280	1.53	1.002	2580

Table 4.9 – *End properties for emulsion polymerisation (9)*

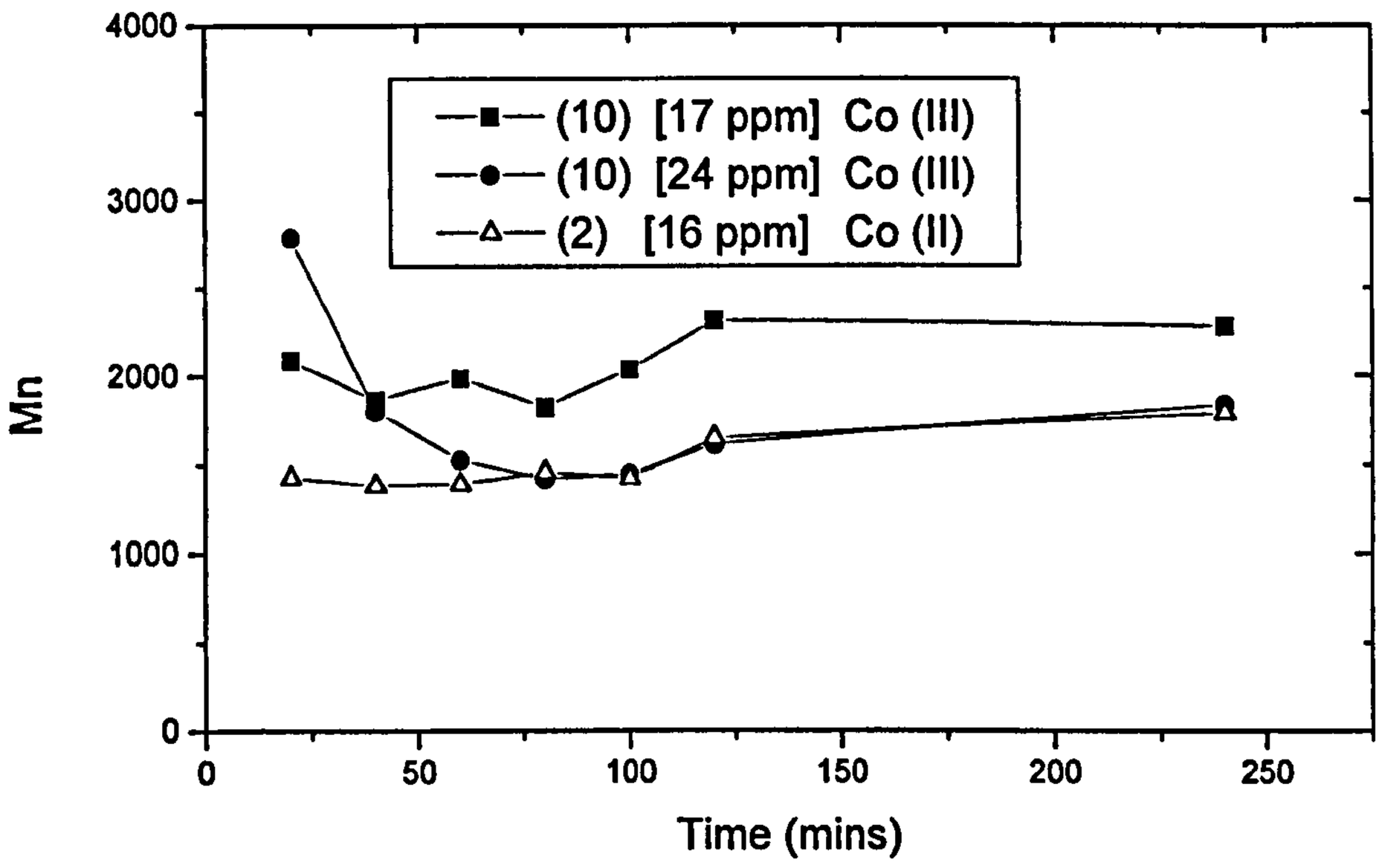


Figure 4.30 – *M_n versus time graph for polymerisations (10)a , (10)b and (10)c*

As for the Co(III) catalysts previously shown, catalyst (10) has a slightly lower effective chain transfer constant in emulsion than its Co(II) counterpart. The chain transfer constant for this catalyst in MMA at 60 °C has been measured as Cs = 8000 and the partitioning was found to be $[(10)]_{MMA}/[(10)]_{aq} = 7.3$ [9]. For the Co(II) analogue the partitioning of catalyst and transfer constant in MMA at 60 °C have been measured as $[(2)]_{MMA}/[(2)]_{aq} = 99.0$ and 14 000 [9]. In this case it

would be predicted that the Co (II) catalyst would have a higher transfer constant in emulsion than the Co (III) and this is the case (Cs^E of 3600 compared to 2400).

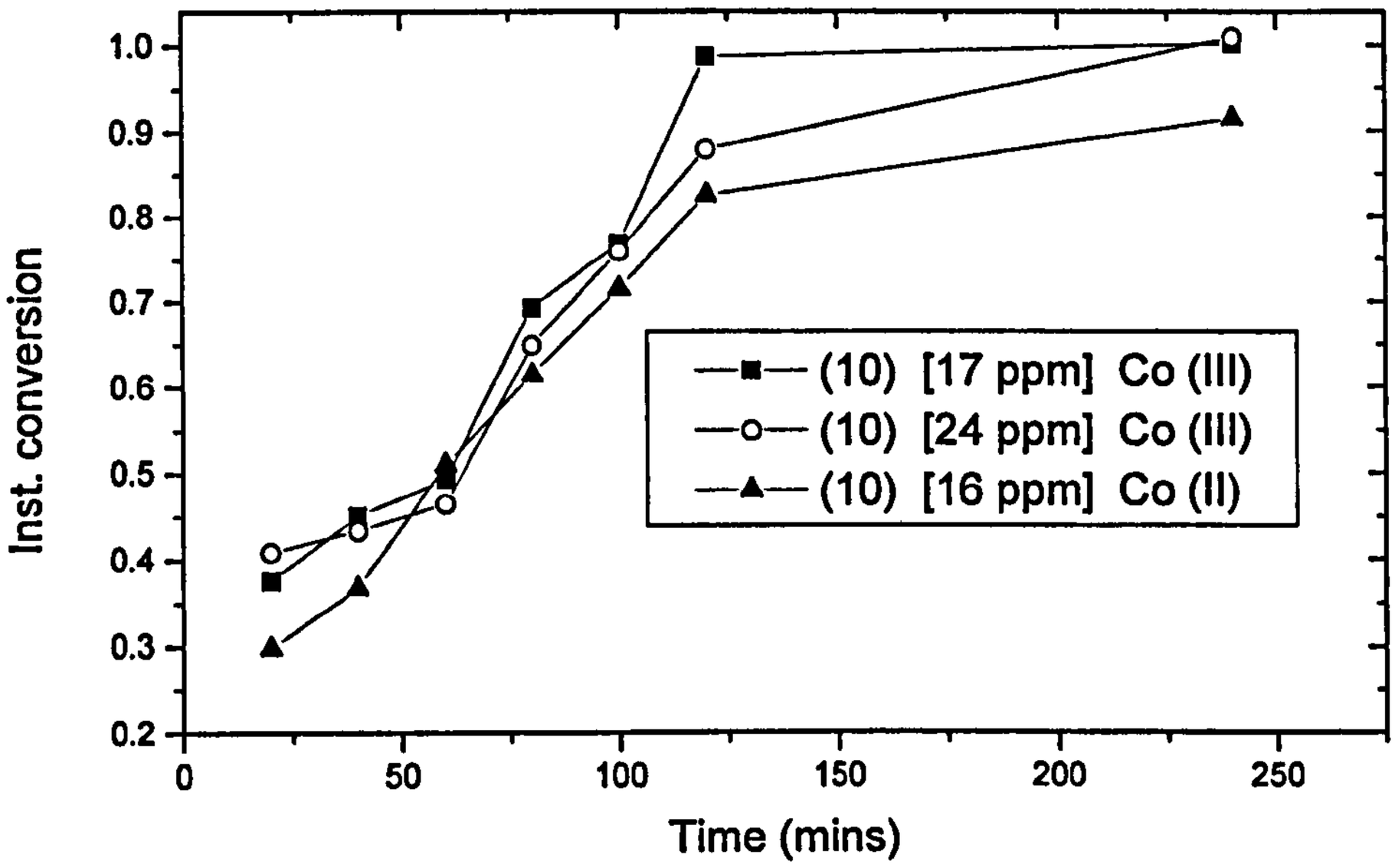


Figure 4.31 – *Instantaneous conversion versus time graph for polymersiations (10)a, (10)b and (10)c*

4.3 Conclusions

Results described in this chapter show that the effectiveness of the CCT emulsion polymerisation process is very dependent on the solublity of the catalyst. The more the CCT agent is soluble in the monomer and hence particle phase the greater the observed transfer constant. If the catalyst is too soluble in the monomer however the observed transfer constant is greatly reduced because the catalyst is unable to transport from the monomer droplets to the particles efficiently. It has also been shown that Co(III) catalysts are less effective at molecular weight reduction in emulsion than their Co(II) equivalents.

4.4 References

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Chapter 5

Experimental

5.1 CCT Emulsion Polymerisations in Chapter 2 (MMA, MMA/BMA, BMA)

Materials

Methyl methacrylate (MMA) {stabilised with 10-100 ppm of hydroquinone monomethyl ether, Aldrich}, Butyl Methacrylate (BMA) {stabilised with 10-100 ppm of hydroquinone monomethyl ether, Aldrich}, Aerosol OT-100 {Sodium bis(2-ethylhexyl) sulfosuccinate) (AOT), Fisons}, 4,4'-azobis(4-cyanovaleric acid) {(CVA) (75% + remainder water, Aldrich} were used as received from the supplier. Water was purified by reverse osmosis. COBF was synthesised by a modified published procedure[1,2]. All liquids were deoxygenated by purging with nitrogen for at least two hours prior to use.

Polymerisations

In a typical polymerisation (polymerisation M1) AOT-100 surfactant (2.00 g) was added to a 1 L flange flask glass reactor under a nitrogen atmosphere. Water (450 mL) was added to the reactor and then heated to the reaction temperature of 80 °C. The mixture was stirred using a turbine impeller at 150 r.p.m.. CVA (2.00 g) was added to the reactor immediately prior to commencement of the monomer/catalyst feed. A solution of the catalytic chain transfer agent (COBF,

0.030 g) in MMA (200 mL) was fed from a Schlenk tube via an FMI pump at a rate of 3.33 mL min^{-1} . Reactions were sampled at 20 minute intervals over the first two hour period and subsequently left for a further two hours before taking a final sample. All samples were analysed for molecular weight and conversion. For reactions where a shot of monomer was required (e.g. polymerisations M7 and M8) 20% of the monomer/catalyst mixture (40 mL) was added directly after the addition of the initiator with the rest of the monomer/catalyst mixture being added at 3.33 mL min^{-1}.

All polymerisations were carried out using a total 200 mL of monomer.

Reactions	MMA (mL)	BMA (mL)
M1 – M8	200	-
MB1 – MB5	80	120
B1 – B5	-	200

Table 5.1 – *Monomer ratios used in Chapter 2 emulsion polymerisations*

5.2. CCT Emulsion Polymerisations in Chapter 3

5.2.1 MMA/HEMA Emulsion Polymerisations

The MMA/HEMA polymerisations were carried out as for pure MMA CCT emulsion reactions. Hydroxyethyl methacrylate (HEMA) was used as obtained (stabilised with 300 ppm hydroquinone monomethyl ether, Aldrich)

Reactions	MMA (mL)	HEMA (mL)
MH1-MH6	135	65
MH7	90	110

Table 5.2 – *Monomer ratios used in section 3.2 emulsion polymerisations*

5.2.2 MMA/Butyl Acrylate Emulsion Polymerisations

The MMA/BA polymerisations were carried out as for pure MMA CCT emulsion reactions. Butyl acrylate (BA) was used as obtained (stabilised with 10-55 ppm mono methyl ether hydroquinone, Aldrich)

Reactions	MMA (mL)	BA (mL)
MA1-MA5	85	115
MA6-MA9	140	60
MA10-MA13	175	25

Table 5.3 – *Monomer ratios used in section 3.3 emulsion polymerisations*

5.2.3 MMA/Methacrylic Acid Emulsion Polymerisations

The MMA/Methacrylic Acid polymerisations were carried out as for pure MMA CCT emulsion reactions. Methacrylic acid was used as obtained (stabilised with 250 ppm hydroquinone monomethyl ether, Aldrich)

Reactions	MMA (mL)	Methacrylic Acid (mL)
MC1-MC4	185	15
MC4-MC6	150	50
MC7-MC8	165	35

Table 5.4 – *Monomer ratios used in section 3.4 emulsion polymerisations*

The methylation of the methacrylic acid containing polymers was performed using a published method[3] with iodomethane (Aldrich, 99.5%) and CsF as a promoter. DMF was used as the solvent (Aldrich, 99.8%). The methylations were performed using a ratio of 2:3:3 on acid groups:CsF:MeI.

5.3 CCT Emulsion Polymerisations in Chapter 4 using Novel Catalysts

All polymerisations were carried out using methyl methacrylate as the monomer using identical conditions to the MMA CCT emulsion polymerisations described in section 5.1.

5.4 Analysis

SEC

Molecular weights were determined by size exclusion chromatography (SEC) using a Polymer Laboratories system with differential refractive index detection. The eluent was THF, with a flow rate of 1.00 mL min^{-1}, with toluene used as an internal flow marker. The column set consisted of Polymer Laboratories 5 -μm guard column (50 x 7.5 mm) and two Polymer Laboratories mixed D columns (300 x 7.5 mm). Data was collected at one point per second and the system was calibrated using 10 Polymer Laboratories PMMA standards and pure MMA dimer, trimer and tetramer. The calibration curve consisted of a log molecular weight expressed as a third order polynomial in the elution volume.

NMR

NMR analysis of each sample was carried out on a 300 MHz Bruker NMR spectrometer using chloroform- *d* (99.8 atom % D, Aldrich)

Differential Scanning Calorimetry (DSC)

The DSC analyses of the polymers synthesised were performed on a Perkin Elmer Differential Scanning Calorimeter (Pyris 1). 7 – 10 mg of each sample were heated at a rate of 10 °C min^{-1}. The samples were heated to above the glass transition temperature and then allowed to cool before the glass transition temperature was accurately measured. The onset and inflection point temperatures of the T_g for each polymer were measured.

Thermal Gravimetric Analysis (TGA)

The thermal behaviour of the PMMA polymers synthesised was measured using a Perkin Elmer Thermogravimetric Analyzer (TGA7). Approximately 10 mg of each sample was heated at a rate of 10 °C min^{-1} under a dry nitrogen atmosphere and the weight loss of the polymer was measured as a function of temperature.

5.5 References

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Appendix

MMA Emulsion Polymerisations

Reaction	wt COBF (g)	ppm COBF	feed conditions	Time (mins)	Inst. Conv	M_n	PDi	Cs^E
M1	0.0300	35.75	100% fed	20	0.385	2250	1.85	1244
				40	0.458	1640	1.96	1706
				60	0.517	1650	1.70	1696
				80	0.735	1630	1.78	1716
				100	0.986	1850	1.77	1512
				120	0.992	2090	1.80	1341
				240	1.003	2120	1.65	1320
M2	0.0210	25.03	100% fed	20	0.446	4880	1.82	819
				40	0.502	3480	1.90	1150
				60	0.565	2900	2.30	1378
				80	0.792	2680	2.05	1500
				100	0.986	3400	1.67	1177
				120	1.009	3410	1.64	1173
				240	1.012	3260	1.77	1226

Reaction	wt COBF (g)	ppm COBF	feed conditions	Time (mins)	Inst. Conv	M_n	PDi	Cs^E
M3	0.0156	18.59	100% fed	20	0.473	5760	1.85	935
				40	0.594	3820	2.23	1410
				60	0.646	3340	2.30	1614
				80	0.944	3670	2.04	1469
				100	1.010	4010	1.91	1344
				120	1.014	4090	1.88	1316
				240	1.015	4030	1.91	1337
M4	0.0139	16.56	100% fed	20	0.475	5280	1.95	1144
				40	0.594	4050	2.01	1492
				60	0.659	2920	2.33	2069
				80	0.939	3520	2.08	1716
				100	0.944	4250	1.76	1422
				120	0.952	4270	1.74	1414
				240	0.977	4160	1.90	1451

Reaction	wt COBF (g)	ppm COBF	feed conditions	Time (mins)	Inst. Conv	M_n	PDi	Cs^E
M5	0.0122	14.53	100% fed	20	0.935	19000	3.18	364
				40	0.972	14600	3.31	472
				60	0.969	14600	2.98	472
				80	1.009	13900	3.09	496
				100	1.017	13800	3.14	498
				120	1.027	13000	2.23	529
				240	1.033	10500	3.91	653
M6	0.00	0.00	100% fed	20	0.923	116000	1.83	-
				40	0.969	124000	1.91	-
				60	0.970	126000	2.37	-
				80	0.985	134000	2.50	-
				100	0.996	128000	2.36	-
				120	0.999	115000	2.03	-
				240	1.001	116000	2.61	-

Reaction	wt COBF (g)	ppm COBF	feed conditions	Time (mins.)	Inst. Conv	M_n	PDi	Cs^E
M7	0.0150	17.87	20%shot/	20	0.285	3130	1.70	1790
			80%fed	40	0.411	2990	1.64	1875
				60	0.616	2880	1.64	1943
				80	0.899	4340	1.63	1290
				100	0.913	4090	1.80	1368
				120	0.923	3900	1.84	1434
				240	0.923	4230	1.79	1322
M8	0.0087	10.37	20%shot/	20	0.216	6500	1.75	1486
			80%fed	40	0.438	5680	1.87	1700
				60	0.689	5820	1.87	1660
				80	0.962	7770	1.88	1242
				100	0.960	6840	2.06	1412
				120	0.968	7120	1.95	1356
				240	0.969	7940	1.80	1215

MMA/BMA Emulsion Polymerisations (50:50)

Reaction	wt COBF (g)	ppm COBF	feed conditions	Time (mins)	Inst. Conv	M_n	PDi	Cs^E
MB1	0.0243	36.04	100% fed	20	0.656	7430	3.02	453
				40	0.698	6650	2.48	506
				60	0.727	5280	2.77	637
				80	0.776	5520	2.09	609
				100	0.974	5130	2.38	565
				120	0.976	5120	2.42	657
				240	0.981	4880	2.35	689
MB2	0.0144	21.36	100% fed	20	0.499	13410	2.35	423
				40	0.525	7890	2.73	720
				60	0.655	6240	2.79	910
				80	0.981	7890	2.19	720
				100	0.998	7620	2.14	745
				120	1.000	7530	2.23	754
				240	1.001	7690	2.11	739

Reaction	wt COBF (g)	ppm COBF	feed conditions	Time (mins)	Inst. Conv	M_n	PDi	Cs^E
MB3	0.0076	11.27	100% fed	20	0.838	21700	2.38	496
				40	1.027	26700	2.06	403
				60	0.998	34200	1.91	314
				80	1.013	34100	1.90	316
				100	1.018	33000	1.96	326
				120	1.016	32800	2.00	328
				240	1.020	33400	1.95	323
MB4	0.0080	11.87	20% shot	20	0.609	18900	2.30	540
			80%fed	40	0.835	15900	2.23	643
				60	0.953	13000	2.23	786
				80	0.959	13000	2.24	783
				100	0.960	13900	2.14	735
				120	0.964	13800	2.15	742
				240	0.965	13300	2.24	766

Reaction	wt COBF (g)	ppm COBF	feed conditions	Time (mins)	inst. conv	M_n	PDi	Cs^E
MB5	0.0000	0.00	100% fed	20	0.854	117000	2.33	-
				40	0.857	110000	2.66	-
				60	0.933	109000	3.00	-
				80	1.008	147000	2.81	-
				100	1.006	157000	2.30	-
				120	1.009	120000	2.75	-
				240	1.023	93700	2.75	-

BMA Emulsion Polymerisations

Reaction	wt COBF (g)	ppm COBF	feed conditions	Time (mins)	inst. conv	M_n	PDi	Cs^E
B1	0.0163	28.88	100% fed	20	0.814	26100	3.04	188
				40	0.830	14500	3.71	341
				60	0.818	9340	3.68	527
				80	0.928	8300	3.71	593
				100	0.959	7990	3.43	617
				120	0.964	8390	3.02	587
				240	0.971	7820	3.62	630

Reaction	wt COBF (g)	ppm COBF	feed conditions	Time (mins)	inst. conv	M_n	PDi	Cs^E
B2	0.0119	21.09	100% fed	20	0.788	30900	3.21	218
				40	0.918	12800	3.47	527
				60	0.928	11200	3.69	603
				80	0.973	11400	3.51	590
				100	0.988	11100	3.64	608
				120	0.985	13000	3.35	518
				240	0.998	11300	3.39	595
B3	0.0062	10.99	100% fed	20	0.765	48700	3.16	266
				40	0.910	56700	2.59	228
				60	0.938	63300	2.49	204
				80	0.988	67100	2.44	193
				100	0.999	65500	2.49	198
				120	1.000	61800	2.54	209
				240	1.009	64400	2.52	201

Reaction	wt COBF (g)	ppm COBF	feed conditions	Time (mins)	inst. conv	M_n	PDi	Cs^E
B4	0.0060	10.63	20% shot	20	0.775	35500	3.50	377
			80%fed	40	0.884	47200	2.42	284
				60	0.952	51300	2.16	261
				80	0.978	47800	2.26	280
				100	0.983	49200	2.24	272
				120	0.983	50900	2.13	263
				240	0.980	45200	2.31	296
B5	0.0000	0.00	100% fed	20	0.816	156000	2.30	-
				40	0.863	143000	2.48	-
				60	0.860	193000	2.40	-
				80	0.867	175000	2.25	-
				100	0.898	157000	2.44	-
				120	0.925	149000	2.47	-
				240	0.939	191000	2.18	-

MMA/HEMA Emulsion Polymerisations (70:30)

Reaction	Wt COBF (g)	ppm COBF	Feed Conditions	Time (mins.)	Inst. Conv.	M_n	PDi	Cs^E
MH1	0.04	45.23	100% fed	20	0.363	1840	1.50	1306
				40	0.454	1640	1.50	1472
				60	0.516	1420	1.54	1690
				80	0.699	1590	1.48	1516
				100	0.847	1840	1.50	1306
				120	0.939	1800	1.49	1340
				240	1.022	1850	1.48	1302
MH2	0.028	35.54	100 % fed	20	0.399	2180	2.58	1411
				40	0.532	1960	2.05	1564
				60	0.624	1960	1.57	1570
				80	0.838	2010	1.79	1530
				100	0.967	1980	1.71	1551
				120	1.005	2570	1.52	1194
				240	1.016	2540	1.72	1209

Reaction	Wt COBF (g)	ppm COBF	Feed Conditions	Time (mins.)	Inst. Conv.	M_n	PDi	Cs^E
MH3	0.0241	30.19	100% fed	20	0.428	2260	2.06	1596
				40	0.528	2360	1.86	1531
				60	0.635	2340	1.58	1538
				80	0.850	2450	1.53	1472
				100	0.979	2590	1.52	1393
				120	1.005	2500	1.59	1440
				240	1.017	2730	1.61	1323
MH4	0.02	19.54	100% fed	20	1.022	15600	2.08	357
				40	1.055	17900	1.87	311
				60	1.017	18400	1.82	303
				80	1.029	19300	1.82	289
				100	1.031	18900	1.85	295
				120	1.030	19500	1.76	285
				240	1.032	16600	1.98	336

Reaction	Wt COBF (g)	ppm COBF	Feed Conditions	Time (mins.)	Inst. Conv.	M_n	PDi	Cs^E
MH5	0.0094	11.78	100% fed	20	1.011	22100	2.19	419
				40	1.041	22600	2.21	410
				60	1.048	26700	2.06	346
				80	1.035	27300	1.99	339
				100	1.035	26500	2.02	349
				120	1.036	27300	1.99	339
				240	1.039	25200	2.02	367
.								
MH6	0.0094	11.78	20% shot	20	0.596	6670	1.80	1386
			80% fed	40	0.827	6760	1.77	1367
				60	0.975	8450	1.65	1094
				80	0.981	7460	1.85	1238
				100	0.981	7670	1.76	1205
				120	0.977	8140	1.69	1136
				240	0.983	7780	1.75	1187

MMA/HEMA Emulsion Polymerisations (50:50)

Reaction	Wt COBF (g)	ppm COBF	Feed Conditions	Time (mins.)	Inst. Conv.	M_n	PDi	Cs^E
MH7	0.028	36.6703	100% fed	20	0.465	3160	1.46	1005
				40	0.615	2230	1.50	1426
				60	0.700	2150	1.44	1473
				80	0.887	2170	1.44	1464
				100	0.937	2230	1.42	1424
				120	1.050	2460	1.33	1288
				240	1.057	2070	1.55	1533

MMA/BA Emulsion Polymerisations (50:50)

Reaction	wt COBF (g)	ppm COBF	feed conditions	Time mins	inst. conv	M_n	PDi	Cs^E
MA1	0.0402	56.10	100% fed	20	0.294	8670	3.66	235
				40	0.300	5290	3.48	385
				60	0.340	4360	2.89	467
				80	0.425	4560	2.53	447
				100	0.546	5390	2.57	378
				120	0.679	6670	2.48	305
				240	0.875	30900	3.41	66
				1200	0.918	56000	2.52	36.4

Reaction	wt COBF (g)	ppm COBF	feed conditions	Time mins	inst. conv	M_n	PDi	Cs^E
MA2	0.0291	40.60	100% fed	20	0.386	14100	2.94	87
				40	0.413	7990	3.22	154
				60	0.415	6820	3.04	180
				80	0.568	7550	2.73	163
				100	0.704	8210	2.51	149
				120	0.787	9840	2.67	125
				150	0.926	13200	2.25	93
				180	0.941	41400	2.82	30
				210	0.956	34900	2.92	35
				270	0.960	45900	2.61	27
				360	0.978	51100	2.48	24
MA3	0.023	35.86	100% fed	20	0.327	11000	3.99	290
				40	0.357	7340	3.93	434
				60	0.364	9250	3.14	344
				80	0.552	18200	2.42	175
				100	0.666	14700	3.13	217
				120	0.874	67200	2.98	47
				240	0.983	70100	2.55	45
				1200	0.990	73500	2.06	43

Reaction	wt COBF (g)	ppm COBF	feed conditions	Time mins	Inst. Conv	M_n	PDi	Cs^E
MA4	0.0150	20.93	100 % fed	20	0.547	54400	2.92	100
				40	0.505	16900	3.26	324
				60	0.497	14300	4.36	380
				80	0.658	18700	2.84	292
				100	0.863	20400	3.93	268
				120	0.915	33300	3.48	164
				240	0.973	79600	3.12	68.6
				1200	0.988	89600	3.11	60.9
MA5	0.0000	0.00	100% fed	20	0.793	201000	3.02	-
				40	0.815	364000	2.32	-
				60	0.816	243000	3.51	-
				80	0.932	363000	2.69	-
				100	0.960	490000	2.27	-
				120	0.926	368000	2.81	-
				1200	0.957	420000	2.54	-

MMA/BA Emulsion Polymerisations (75:25)

Reaction	wt COBF (g)	ppm COBF	feed conditions	Time (mins.)	inst. Conv	M_n	PDi	Cs^E
MA6	0.0230	32.09	100% fed	20	0.378	6940	2.23	513
				40	0.396	3410	3.74	1043
				60	0.426	3270	2.76	1090
				80	0.578	3310	2.46	1074
				100	0.650	4260	2.23	835
				120	0.662	5780	1.94	616
				240	0.997	10700	1.87	334
MA7	0.015	20.93	100% fed	20	0.529	15200	2.69	358
				40	0.529	8370	3.13	652
				60	0.542	6670	3.12	819
				80	0.737	7080	2.78	770
				100	0.899	9110	2.46	599
				120	0.987	10700	2.55	511
				240	1.010	13900	2.41	393

Reaction	wt COBF (g)	ppm COBF	feed conditions	Time (mins)	inst. conv	M_n	PDi	Cs^E
MA8	0.008	11.16	100% fed	20	0.290	19000	2.48	539
				40	0.536	15200	2.87	675
				60	0.734	14000	2.82	719
				80	0.989	18800	2.59	545
				100	1.021	22200	2.58	461
				120	1.022	25100	2.39	408
				240	1.021	26400	2.37	388
MA9	0.000	0.00	100% fed	20	1.011	133000	3.40	-
				40	1.022	224000	2.34	-
				60	0.935	184000	2.95	-
				80	0.939	227000	2.45	-
				100	1.040	212000	2.74	-
				120	1.032	196000	2.77	-
				240	1.041	177000	3.14	-

MMA/BA Emulsion Polymerisations (90:10)

Reaction	wt COBF (g)	ppm COBF	feed conditions	Time (mins)	inst. Conv	M_n	PDi	Cs^E
MA10	0.0316	38.89	100% fed	20	0.364	4440	1.70	596
				40	0.377	2720	1.75	974
				60	0.412	2230	2.15	1187
				80	0.568	2280	2.07	1161
				100	0.692	1680	2.40	1573
				120	0.931	2270	2.19	1166
				240	1.037	3120	1.87	848
MA11	0.0224	27.57	100% fed	20	0.496	6480	1.95	576
				40	0.532	4610	1.92	809
				60	0.588	3250	2.45	1147
				80	0.816	2730	1.85	1364
				100	0.941	4640	1.74	804
				120	1.014	3180	2.12	1174
				240	1.008	4560	1.76	818

Reaction	wt COBF (g)	ppm COBF	feed conditions	Time (mins)	inst. Conv	M_n	PDi	Cs^E
MA12	0.0101	12.43	100% fed	20	0.952	22700	2.20	365
				40	0.971	25400	2.33	325
				60	0.947	28500	2.37	290
				80	1.034	28800	2.42	287
				100	1.035	29200	2.35	283
				120	1.049	30600	2.31	270
				240	1.042	30100	2.30	275
MA13	0	0.00	100% fed	20	0.945	118000	2.31	-
				40	0.954	127000	2.21	-
				60	0.926	129000	2.60	-
				80	1.044	131000	2.70	-
				100	1.050	128000	2.79	-
				120	1.053	127000	2.81	-
				240	1.060	133000	2.70	-

MMA/Methacrylic Acid Emulsion Polymerisations (90:10)

Reaction	wt COBF (g)	ppm COBF	feed conditions	Time (mins)	inst. Conv	M_n	PDi	Cs^E
MC1	0.0203	23.7266	100% fed	20	0.350	3290	3.19	1265
				40	0.524	2960	2.60	1408
				60	0.731	2900	2.49	1439
				80	0.945	2820	2.68	1474
				100	0.973	390	2.56	1307
				120	0.994	3180	2.63	1308
				240	1.038	3150	3.32	1320
MC2	0.0325	37.9859	100% fed	20	0.387	3370	2.18	772
				40	0.435	1720	1.78	1516
				60	0.514	1300	1.79	2010
				80	0.961	1640	1.84	1584
				100	0.951	1960	1.77	1329
				120	0.972	2070	1.81	1259
				240	1.005	2150	1.73	1211

Reaction	wt COBF (g)	ppm COBF	feed conditions	Time (mins)	inst. Conv	M_n	PDi	Cs^E
MC3	0.015	17.53	100% fed	20	0.571	6210	2.10	908
				40	0.651	4600	2.09	1226
				60	0.971	4500	1.85	1253
				80	1.008	4390	1.88	1284
				100	1.046	4610	1.83	1222
				120	1.038	4520	1.84	1248
				240	1.036	4630	1.81	1217
MC4	0.0115	13.4412	100% fed	20	0.991	7870	2.85	933
				40	1.003	6660	2.53	1104
				60	0.979	6520	2.37	1127
				80	0.985	6470	2.43	1136
				100	1.049	6350	2.48	1158
				120	1.046	6240	2.53	1178
				240	1.053	5660	2.42	1298

MMA/Methacrylic Acid Emulsion Polymerisations (70:30)

Reaction	wt COBF (g)	ppm COBF	Time (mins.)	inst. Conv	M_n (NMR)	M_n (GPC)	CsE NMR	Cs^E GPC
MC5	0.035	39.15	20	0.959	-	-	-	-
			40	0.996	-	-	-	-
			60	1.000	-	-	-	-
			80	1.005	-	-	-	-
			100	1.005	-	-	-	-
			120	1.004	-	-	-	-
			240	1.007	10400	17500	235	140
MC6	0.021	23.49184	20	0.953	-	-	-	-
			40	1.010	-	-	-	-
			60	1.022	-	-	-	-
			80	1.025	-	-	-	-
			100	1.028	-	-	-	-
			120	1.027	-	-	-	-
			240	1.027	11200	19400	366	211

Reaction	wt COBF (g)	ppm COBF	Time (mins)	inst. Conv	M_n (NMR)	M_n (GPC)	CsE NMR	Cs^E GPC
MC7	0.01	11.19	20	0.992	-	-	-	-
			40	1.032	-	-	-	-
			60	1.039	-	-	-	-
			80	1.039	-	-	-	-
			100	1.054	-	-	-	-
			120	1.052	-	-	-	-
			240	1.041	15200	18700	564	459

MMA/Methacrylic Acid Emulsion Polymerisations (80:20)

Reaction	wt COBF (g)	ppm COBF	Time (mins)	inst. Conv	M_n (GPC)	PDi	Cs^E
MC8	0.034	38.74	20	0.971	-	-	-
			40	0.997	-	-	-
			60	1.016	-	-	-
			80	1.016	-	-	-
			100	1.013	-	-	-
			120	1.026	-	-	-
			240	1.049	16718	2.12	150

Reaction	wt COBF (g)	ppm COBF	Time (mins)	inst. Conv	M_n (GPC)	PDi	Cs^E
MC9	0.0216	24.6156	20	0.997	-	-	-
			40	1.037	-	-	-
			60	1.043	-	-	-
			80	1.058	-	-	-
			100	1.070	-	-	-
			120	1.051	-	-	-
			240	1.064	19500	2.36	202

New Catalysts in emulsion

Emulsion Polymerisations Using Co(II) Catalysts

Reaction	Wt Catalyst (g)	ppm	Time (mins.)	Inst. Conv.	M_n	PDi	Cs^E
(1) a	0.0177	19.85	20	0.309	1960	1.98	2578
			40	0.437	1860	1.90	2705
			60	0.526	1760	1.93	2871
			80	0.716	1870	1.93	2698
			100	0.849	2000	1.90	2522
			120	0.988	2190	1.90	2303
			240	1.017	2260	1.88	2233

Reaction	Wt Catalyst (g)	ppm	Time (mins.)	Inst. Conv.	M_n	PDi	Cs^E
(2) a	0.0155	16.41	20	0.298	1430	1.37	4273
			40	0.368	1380	1.43	4415
			60	0.510	1390	1.41	4387
			80	0.615	1460	1.40	4182
			100	0.715	1430	1.52	4279
			120	0.825	1650	1.45	3700
			240	0.915	1790	1.48	3406
(2) b	0.034	35.48	20	0.091	694	1.28	4065
			40	0.163	710	1.25	3974
			60	0.185	711	1.29	3968
			80	0.226	729	1.28	3870
			100	0.307	724	1.29	3897
			120	0.355	756	1.36	3732
			240	0.527	789	1.41	3576

Reaction	Wt Catalyst (g)	ppm	Time (mins.)	Inst. Conv.	M_n	PDi	Cs^E
(3)	0.0294	25.48	20	0.902	20700	1.818	189
			40	0.922	22000	1.896	178
			60	0.885	18500	2.302	212
			80	1.008	22900	2.049	171
			100	0.996	19800	1.669	198
			120	1.019	21800	1.643	180
			240	1.023	20700	1.77	189

Reaction	Wt Catalyst (g)	ppm	Time (mins.)	Inst. Conv.	M_n	PDi	Cs^E
(4)	0.0305	25.285	20	0.901	29200	1.723	135
			40	0.928	26300	1.923	150
			60	0.903	30300	1.681	130
			80	0.991	27200	1.901	145
			100	0.960	28400	1.865	139
			120	1.015	27500	2.057	144
			240	1.044	29200	1.896	135

Reaction	Wt Catalyst (g)	ppm	Time (mins.)	Inst. Conv.	M_n	PDi	Cs^E
(5) a	0.0301	32.14	20	0.275	1160	1.52	2690
			40	0.352	885	2.10	3520
			60	0.407	1140	1.83	2739
			80	0.570	1120	2.19	2776
			100	0.741	1600	2.19	1951
			120	0.902	1730	2.23	1801
			240	1.030	1750	2.20	1777
(5) b	0.015	16.02	20	0.320	1980	1.93	3162
			40	0.456	2270	1.72	2752
			60	0.456	2870	1.91	2177
			80	0.666	2630	1.81	2375
			100	1.002	3900	1.77	1605
			120	1.022	3800	1.80	1643
			240	1.022	3760	1.81	1664

Reaction	Wt Catalyst (g)	ppm	Time (mins.)	Inst. Conv.	M_n	PDi	Cs^E
(5) c	0.0106	11.32	20	0.451	4370	1.558	2024
			40	0.523	4130	1.627	2142
			60	0.601	4830	1.626	1833
			80	0.998	5750	1.624	1540
			100	1.017	5300	1.741	1670
			120	1.022	5210	1.763	1698
			240	1.022	4990	1.835	1774

Reaction	Wt Catalyst (g)	ppm	Time (mins.)	Inst. Conv.	M_n	PDi	Cs^E
(6)	0.0294	23.36	20	0.856	41700	1.65	103
			40	0.911	54800	1.63	78
			60	0.877	56400	1.75	76
			80	0.898	50200	2.07	85
			100	0.950	50300	2.05	85
			120	1.014	53300	1.97	80
			240	1.003	53200	1.98	80

Reaction	Wt Catalyst (g)	ppm	Time (mins.)	Inst. Conv.	M_n	PDi	Cs^E
(7) a	0.0395	25.85	20	0.517	8010	2.01	484
			40	0.905	10100	1.50	384
			60	0.862	11200	1.47	346
			80	0.969	10100	1.64	383
			100	0.981	10100	1.44	384
			120	0.989	10100	1.49	384
			240	0.979	11300	1.56	344
(7) b	0.0286	18.71	20	0.506	7520		712
			40	0.872	14100		380
			60	0.897	15200		353
			80	0.972	16200		331
			100	0.981	17600		303
			120	0.991	16400		326
			240	0.990	17300		309

Reaction	Wt Catalyst (g)	ppm	Time (mins.)	Inst. Conv.	M_n	PDi	Cs^E
(7)	0.0109	23.77	20	0.927	16200	1.54	261
			40	0.995	24600	1.55	171
			60	0.999	26300	1.72	160
Low solids 60 ml MMA			80	1.000	32700	1.51	129
			100	0.998	24700	1.77	170
			120	1.005	33200	1.53	127
			240	1.012	29800	1.62	141

Emulsion Polymerisations Using Co(III) catalysts

Reaction	Wt Catalyst (g)	ppm	Time (mins.)	Inst. Conv.	M_n	PDi	Cs^E
(8)	0.0291	31.44	20	0.902	13100	2.746	243
			40	0.935	13400	2.960	238
			60	0.955	9950	2.729	320
			80	0.965	13800	2.783	231
			100	0.990	10700	2.874	299
			120	1.016	8950	2.872	356
			240	1.025	11900	2.834	268

Reaction	Wt Catalyst (g)	ppm	Time (mins.)	Inst. Conv.	M_n	PDi	Cs^E
(9)	0.0305	35.47	20	0.540	4390	1.68	643
			40	0.579	3380	1.82	836
			60	0.615	2810	1.71	1003
			80	0.845	2660	1.64	1063
			100	1.035	2780	1.59	1017
			120	1.038	2610	1.58	1083
			240	1.043	3130	1.66	903

Reaction	Wt Catalyst (g)	ppm	Time (mins.)	Inst. Conv.	M_n	PDi	Cs^E
(10) a	0.0248	24.11	20	0.409	2790	2.26	1487
			40	0.434	1800	2.47	2304
			60	0.465	1530	1.91	2721
			80	0.649	1420	1.63	2926
			100	0.759	1450	1.56	2863
			120	0.879	1610	1.57	2572
			190	1.000	1680	1.53	2474
			240	1.005	1840	1.51	2260
			300	1.009	1780	1.55	2331

Reaction	Wt Catalyst (g)	ppm	Time (mins.)	Inst. Conv.	M_n	PDi	Cs^E
(10) b	0.0175	17.01	20	0.376	2090	1.63	2815
			40	0.451	1860	1.53	3158
			60	0.493	1990	1.50	2960
			80	0.693	1830	1.53	3224
			100	0.768	2040	1.54	2887
			120	0.987	2320	1.50	2542
			240	1.002	2280	1.53	2580